

Crystal and Molecular Structures of 3-Acetyl-5-[2-(3-ethyl-2-benzothiazolidene)]-ethylidenerhodanine and its Lithium and Sodium Salts. Layered Organic–Inorganic Structures

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Abstract

An X-ray diffraction study of the crystals of 5-[2-(3-ethyl-2-benzothiazolidene)]ethylidenerhodanine *N*-acetic acid (1, solvate with dimethylsulfoxide), lithium 5-[2-(3-ethyl-2-benzothiazolidene)]ethylidenerhodanine *N*-acetate (2, solvate with water and dimethylformamide) and sodium 5-[2-(3-ethyl-2-benzothiazolidene)]ethylidenerhodanine *N*-acetate (3, octahydrate) have been carried out at 295 K. Crystal data for (1): $C_{16}H_{14}N_2O_3S_3 \cdot C_2H_6OS$, $M_r = 456.6$, triclinic, $a = 7.664(6)$, $b = 9.874(8)$, $c = 14.851(8)$ Å, $\alpha = 101.71(5)$, $\beta = 90.45(5)$, $\gamma = 102.27(5)^\circ$, $V = 1074(1)$ Å³, space group $P1$, $Z = 2$, $F(000) = 476$, $D_x = 1.412$ g cm⁻³, $\mu(\text{Mo } K\alpha) = 0.469$ mm⁻¹, $R = 0.0698$ for 1688 reflections with $F > 6\sigma(F)$; for (2): $\text{Li}^+ \cdot C_{16}H_{13}N_2O_3S_3 \cdot 2H_2O \cdot 1.5C_3H_7NO$, $M_r = 530.1$, triclinic, $a = 7.249(5)$, $b = 10.773(6)$, $c = 16.433(13)$ Å, $\alpha = 87.66(6)$, $\beta = 85.22(6)$, $\gamma = 77.04(6)^\circ$, $V = 1246(1)$ Å³, space group $P1$, $Z = 2$, $F(000) = 556$, $D_x = 1.413$ g cm⁻³, $\mu(\text{Mo } K\alpha) = 0.342$ mm⁻¹, $R = 0.0551$ for 2360 reflections with $F > 6\sigma(F)$; for (3): $\text{Na}^+ \cdot C_{16}H_{13}N_2O_3S_3 \cdot 8H_2O$, $M_r = 544.6$, monoclinic, $a = 46.209(12)$, $b = 7.005(3)$, $c = 16.583(8)$ Å, $\beta = 109.45(4)^\circ$, $V = 5061(6)$ Å³, space group $C2/c$, $Z = 8$, $F(000) = 2288$, $D_x = 1.429$ Mg m⁻³, $\mu(\text{Mo } K\alpha) = 0.365$ mm⁻¹, $R = 0.0440$ for 2680 reflections with $F > 6\sigma(F)$. Crystals (1) and (2) are built up of stacks of head-to-tail oriented molecules and anions, respectively, which have alternating interplanar separations of 3.41(1) and 3.46(1) Å for (1), and 3.38(1) and 3.45(1) Å for (2) (so-called H aggregation of dye). The Li⁺ cations and solvent molecules form the cationic layers in crystal (2), alternating with the anionic layers along the *c* direction. The shifted head-to-head oriented anions in crystal (3) form uniform stacks along the *b* axis at the interplanar separation of 3.39(1) Å (so-called J aggregation of dye). The stacks are arranged in bilayers with the O atoms on the outer surfaces of the bilayers. The inorganic layers situated between

the anionic organic bilayers consist of extended chains of distorted edge-shared polyhedra of Na⁺ cations and water molecules. The O atoms on the outer surfaces of the bilayers do not participate in the direct ionic interactions with the Na⁺ cations. The structure and stability of layered organic–inorganic structures with internal surfaces are discussed by means of the crystal structures of (1)–(3) and literature data.

1. Introduction

Compounds built of alternate extended two-dimensional organic and inorganic motifs can form quite a widespread type of intergrowth structure. Special interest in such arrangements is presently focused on the structures of the internal surfaces and onto the mutual influence of organic and inorganic layers, because of attempts to understand heterogeneous catalysis on a molecular level (Somorjai, 1994), structure–property relations at the dye-sensitized semiconductor surface in a new type of photovoltaic cell (Grätzel, 1991) and storage of information by molecules which are fixed in inclusion compounds (Miyata & Miki, 1993).

The design of organic–inorganic crystals with nonlinear optics properties based on 2-amino-5-nitropyridinium salts in different inorganic matrices (Pecaut & Masse, 1993; Bagieu-Beucher, Masse & Tranqui, 1991; Masse & Zyss, 1991) exemplify the use of the mutual structural influence of organic and inorganic counterparts in such composite structure. For example, the influence of the inorganic arrangement changes the charge-transfer properties in the organic part of the structure, while the latter by symmetry and alignment of the organic molecules serves as a promoter of polar crystal symmetry.

The possibility of changing the structural and spectral properties of organic and metal-complex dyes by optimization of the inorganic support was especially interesting for us because such dyes are promising candidates as sensitizers for adjusting band-gap metal

Table 1. *Experimental details*

	(1)	(2)	(3)
Crystal data			
Chemical formula	C ₁₆ H ₁₄ N ₂ O ₃ S ₃ ·C ₂ H ₆ OS	Li ⁺ ·C ₁₆ H ₁₃ N ₂ O ₃ S ₃ ⁻ ·1.5C ₃ H ₇ NO·2H ₂ O	Na ⁺ ·C ₁₆ H ₁₃ N ₂ O ₃ S ₃ ⁻ ·.8H ₂ O
Chemical formula weight	456.6	530.1	544.6
Cell setting	Triclinic	Triclinic	Monoclinic
Space group	P1	P1	C2/c
<i>a</i> (Å)	7.664 (6)	7.249 (5)	46.209 (12)
<i>b</i> (Å)	9.874 (8)	10.773 (6)	7.005 (7)
<i>c</i> (Å)	14.851 (8)	16.433 (13)	16.583 (8)
α (°)	101.71 (5)	87.66 (6)	90.0
β (°)	90.45 (5)	85.22 (6)	109.45 (4)
γ (°)	102.27 (5)	77.04 (6)	90.0
<i>V</i> (Å ³)	1074 (1)	1246 (2)	5061 (6)
<i>Z</i>	2	2	8
<i>D_x</i> (Mg m ⁻³)	1.412	1.413	1.429
Radiation type	Mo K α	Mo K α	Mo K α
Wavelength (Å)	0.71073	0.71073	0.71073
No. of reflections for estimation of cell parameters	264	282	307
θ range (°)	3.15–22.5	3.55–24.2	3.55–24.2
μ (mm ⁻¹)	0.469	0.342	0.365
<i>F</i> (000)	476	556	2288
Temperature (K)	295	295	295
Crystal form	Needles	Plate	Plate
Crystal size (mm)	0.30 × 0.03 × 0.03	0.50 × 0.10 × 0.01	0.40 × 0.10 × 0.01
Crystal colour	Violet	Red	Golden-red
Detector distance (mm)	90	80	80
$\varphi_{\text{start}} - \varphi_{\text{end}}$ (°), $\Delta\varphi$ (°)	0–180, 2	0–180, 2	0–181.5, 1.5
Exposure time (min per exposure)	6	10	10
No. of patterns	92	92	121
Data collection			
Diffractometer	Scanner Stoe IPDS	Scanner Stoe IPDS	Scanner Stoe IPDS
Data collection method	Oscillation	Oscillation	Oscillation
Absorption correction	None	None	None
No. of measured reflections	4634	6894	14 033
No. of independent reflections	2553	3622	3770
No. of observed reflections	1688	2360	2680
Criterion for observed reflections	$ F > 6\sigma F $	$ F > 6\sigma F $	$ F > 6\sigma F $
<i>R</i> _{int}	0.0599	0.0275	0.041
θ_{max} (°)	22.5	24.2	24.2
Range of <i>h</i> , <i>k</i> , <i>l</i>	–8 → <i>h</i> → 8 –10 → <i>k</i> → 10 –14 → <i>l</i> → 15	–7 → <i>h</i> → 7 –12 → <i>k</i> → 11 –18 → <i>l</i> → 18	–49 → <i>h</i> → 49 –7 → <i>k</i> → 7 –18 → <i>l</i> → 18
Refinement			
Refinement on	<i>F</i>	<i>F</i>	<i>F</i>
<i>R</i>	0.0698	0.0551	0.0440
<i>wR</i>	0.0673	0.0567	0.0447
<i>S</i>	1.40	1.13	2.89
No. of reflections used in refinement	1688	2360	2680
No. of parameters used	253	331	359
Reflections/parameters ratio	6.7:1	7.1:1	7.5:1
H-atom treatment	Refined, riding	Refined, riding	Refined, riding
Weighting scheme	Unit weights	Unit weights	Unit weights
(Δ/σ) _{max}	0.013	0.44	0.38
$\Delta\rho_{\text{max}}$ (e Å ⁻³)	0.52	0.43	0.19
$\Delta\rho_{\text{min}}$ (e Å ⁻³)	–0.32	–0.42	–0.23
Extinction method	None	None	None
Source of atomic scattering factors	<i>International Tables for X-ray Crystallography</i> (1974, Vol. IV)	<i>International Tables for X-ray Crystallography</i> (1974, Vol. IV)	<i>International Tables for X-ray Crystallography</i> (1974, Vol. IV)

oxide supports (Grätzel, 1991). The physico-chemical properties of organic dyes may depend critically on the character of intermolecular association and interaction with the inorganic support. The aggregation of molecules of cyanine dyes (Zollinger, 1987) determines their

spectral absorption properties as coatings on inorganic surfaces. In the spectroscopy, the parallel side-by-side alignment of chromophores exhibiting a hypsochromic (blue) shift is known as 'H aggregation' and antiparallel head-to-tail alignment of chromophores with a batho-

chromic (red) shift is known as 'J aggregation'. The J *versus* H aggregation has been discussed, *e.g.* by Maskasky (1991) or Okuyama (1993). Differences in colour due to different molecular aggregations and a preferred orientation of crystallites or molecules on substrate surface were observed using X-ray powder diffraction and FT-IR studies of thin films of the triclinic form of 3-ethyl-5-[2-(3-ethyl-2-benzothiazolinylidene)ethylidene]rhodanine (4) on the silicon and oxide substrates (Hattori *et al.*, 1990). This dye molecule is closely related to (1). The monoclinic modification of (4) has a different colour and morphology, as found by X-ray powder diffraction studies of (4) obtained by condensation on heated substrate (Hertz, Böttcher, Fischer & Fichtner, 1991). (The triclinic modification forms violet needles and the orthorhombic green plates.) The parallel orientation of the long molecular axes, which is favourable for the J aggregation, was suggested from the X-ray powder diffraction study of the composite Langmuir-Blodgett (LB) films of cyanine dye, 5,5-dichloro-3,3,9-triethylthiacarbocyanine chloride, and stearic acid (Nakano, Shimizu, Takahashi, Nakahar & Fukuda, 1988). A brick model with parallel orientation of molecules was used for the explanation of structure and stability of merocyanine J aggregates in monomolecular and LB films (Kawaguchi & Iwata, 1990). ESR studies of mixed LB films of merocyanine dyes and arachidic acid indicated the formation of two stable cationic and anionic radicals due to intermolecular charge transfer in the J aggregates (Kuroda *et al.*, 1991).

The aim of our study of the crystal structure of merocyanine dye, 5-[2-(3-ethyl-2-benzothiazolidene)ethylidene]rhodanine *N*-acetic acid, and its Li⁺ and Na⁺ salts (crystals 1, 2 and 3, respectively; all crystal structures contain solvate molecules) was to elucidate the character of association of molecules in the crystals, which strongly determines the optical properties of this dye both in the bulk form and in thin films. The distinct separation of organic and inorganic layers in the crystals (2) and (3) led us to the more general discussion of the structure of layered organic-inorganic crystals.

2. Experimental

Diffraction data for the crystals (1)–(3) were collected at 295 K on the Scanner STOE IPDS using MoK α radiation with a graphite monochromator ($\lambda = 0.71073$ Å, weighted K α_1 and K α_2 radiation). Experimental details of the X-ray structure determination of (1)–(3) are given in Table 1. Red plate-like single crystals of (2) and golden-red plate-like crystals of (3) quickly lose crystal water, becoming black and amorphous. For the measurements of X-ray intensities the crystals of (2) and (3) were sealed in glass capillaries with the mother liquid and mounted on the scanner. Five successive exposures at the rotation angles $\varphi = 0, 30, 60,$

90 and 120° (10 min per exposure) were used for the estimation of the unit-cell parameters of (1), (2) and (3) with 264, 282 and 307 reflections, respectively. For (1) and (2) the unit cells determined by the *CELL* routine and Delauney reduction were used for the subsequent structure refinements. For (3) the indexing routine gave a triclinic unit cell with $a = 7.005$ (3), $b = 16.583$ (8), $c = 23.368$ (12) Å, $\alpha = 109.22$ (4), $\beta = 98.61$ (4), $\gamma = 90.01$ (3)°, $V = 2530$ (3) Å³. From the analysis of extinctions and symmetry of the diffraction patterns, the monoclinic space group *C2/c* was chosen with $a = 46.209$ (12), $b = 7.005$ (3), $c = 16.583$ (8) Å, $\beta = 109.45$ (4)° and $V = 5061$ (6) Å³. The oscillation mode was used for the data collections. The observed reflections showed effective mosaic spreads of 0.018 for (1), 0.048 for (2) and 0.028 for (3). The automatic mean profile analysis was used. A minimum of 50 and a maximum of 200 control reflections with $I/\sigma(I) = 6.0$ were used to scale the separate image-plate patterns against each other for all the crystals (1), (2) and (3). The index ranges were $-8 < h < 8$, $-10 < k < 10$, $-14 < l < 15$ for (1), $-7 < h < 7$, $-12 < k < 11$, $-18 < l < 18$ for (2) and $-49 < h < 49$, $-7 < k < 7$, $-18 < l < 18$ for (3). The structures were solved by direct methods and refined by full-matrix least-squares (refinement on F , unit weights) with anisotropic displacement parameters for all non-H atoms. The relatively high cut-off level $F > 6\sigma(F)$ is due to the underestimation of standard deviations of weak intensities in the image plate scanner.

A molecule of dimethylsulfoxide was found in structure (1). Crystal (2) contains two molecules of crystal water and two molecules of dimethylformamide, one of which is disordered around the inversion centre at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. The occupancies of atoms of disordered molecules of dimethylformamide were chosen to be 0.5 judging from the displacement parameters. The position of the H atoms of the water molecule [O(7)] was not localized. Nine molecules of crystal water were found during the refinement of (3), two of which are located at special positions on the twofold axes. The positions of H atoms of molecule (1) and the anions in (2) and (3) were assigned geometrically at every stage of refinement and included in the structure-factor calculations (riding model, fixed values of U_{iso}). The positions of the H atoms of water molecules in (2) and (3) were determined from the difference-Fourier syntheses and refined at the fixed values of isotropic thermal parameters. No absorption correction was applied. Programs *SHELXTL-Plus* (Sheldrick, 1990) were used for data reduction, structure solution and refinement.*

* Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and mean-plane equations have been deposited with the IUCr (Reference: AB0334). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

3. Results and discussion

3.1. Molecular structure

Final positional and displacement parameters of the atoms in (1)–(3) are listed in Tables 2–4 and distances and bond angles are given in Table 5. The molecular structures and the orientation of the substituents are shown in Figs. 1–3. The distributions of bond lengths and angles at the C(16) atom clearly indicate the non-ionized HO-acid form of the molecules in crystal (1) and an ionized acetate form of the anions in crystals (2) and (3). The N(1)—ethyl and N(2)—acetyl [or N(2)—acetato] substituents have a different mutual orientation to the molecular planes in the studied structures: *cis* in (1), *trans* in (2) and (3) [the torsion angles C(1)—N(1)—C(13)—C(14) and C(11)—N(2)—(15)—C(16) are 88.5(8) and 96.1(8)° in (1), 84.9(5) and –82.0(5)° in (2), and –78.7(3) and 68.4(3)° in (3)]. These substituents can freely rotate round the N(1)—C(13) and N(2)—C(15) bonds and do not hinder the mutual approach of molecules or anions in the crystals.

The molecule in (1) and anions in (2) and (3) are only approximately coplanar, with a remarkable increase of the planarity of organic species in the series (1) < (2) < (3). The planarity of the whole molecular framework is an indication of the π -delocalization over the central ethylidene C(1)··C(2)··C(3)··C(4) bridge, where the lengths of all three C—C bonds (Table 5) are intermediate between the lengths of conjugated ordinary bonds Csp^2-Csp^2 and conjugated double bonds $Csp^2=Csp^2$ in the moiety C=C—C=C [1.455 and 1.330 Å, respectively (Allen, Kennard, Watson, Brammer & Orpen, 1987)]. Consequently, the π -delocalization through the organic framework increases in the sequence (1) < (2) < (3).

A π -delocalization through the ethylidene bridge between the electron-donating benzothiazole and electron-accepting rhodanine chromophores was also found in the crystal of 3-ethyl-5-[2-(3-ethyl-2-benzothiazolinylidene)ethylidene]rhodanine (4) (Bai, Chang & Xu, 1983).

The lengths of endocyclic S—C bonds at the S(1) and S(2) atoms of 1.717(5)–1.75(1) Å are between the S—C bond length of 1.712 Å in thiophene and 1.768 Å in phenothiazine (Allen, Kennard, Watson, Brammer & Orpen, 1987), which does not exclude the participation

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for (1)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
S(1)	0.2796 (3)	–0.1197 (2)	0.0120 (2)	0.065 (1)
S(2)	0.1157 (3)	0.4336 (2)	0.0777 (2)	0.067 (1)
S(3)	0.0399 (4)	0.6948 (3)	0.1962 (2)	0.090 (1)
O(1)	0.0882 (9)	0.2380 (6)	0.2771 (4)	0.072 (3)
O(2)	0.3459 (10)	0.6074 (7)	0.3643 (5)	0.085 (3)
O(3)	0.1654 (9)	0.6769 (7)	0.4731 (4)	0.089 (3)
N(1)	0.2844 (9)	–0.0388 (7)	–0.1413 (5)	0.058 (3)
N(2)	0.0587 (9)	0.4526 (7)	0.2490 (5)	0.061 (3)
C(1)	0.2522 (11)	0.0048 (8)	–0.0527 (6)	0.055 (4)
C(2)	0.2027 (11)	0.1309 (8)	–0.0127 (6)	0.058 (4)
C(3)	0.1694 (11)	0.1655 (8)	0.0794 (6)	0.059 (4)
C(4)	0.1265 (12)	0.2875 (8)	0.1258 (6)	0.059 (4)
C(5)	0.3387 (12)	–0.1694 (9)	–0.1618 (7)	0.062 (4)
C(6)	0.3377 (11)	–0.2284 (9)	–0.0849 (6)	0.061 (4)
C(7)	0.3840 (12)	–0.3603 (9)	–0.0908 (7)	0.072 (4)
C(8)	0.4270 (13)	–0.4263 (10)	–0.1754 (9)	0.085 (5)
C(9)	0.4283 (13)	–0.3670 (10)	–0.2512 (8)	0.082 (5)
C(10)	0.3817 (12)	–0.2371 (9)	–0.2467 (7)	0.073 (4)
C(11)	0.0929 (12)	0.3144 (9)	0.2210 (7)	0.062 (4)
C(12)	0.0706 (12)	0.5303 (8)	0.1818 (7)	0.065 (4)
C(13)	0.2634 (13)	0.0424 (9)	–0.2125 (6)	0.073 (4)
C(14)	0.4348 (16)	0.1487 (10)	–0.2189 (7)	0.105 (6)
C(15)	0.0306 (12)	0.5114 (9)	0.3438 (6)	0.064 (6)
C(16)	0.2006 (15)	0.6035 (9)	0.3928 (6)	0.066 (4)
S(4)	0.3645 (5)	0.1395 (5)	0.4898 (2)	0.105 (2)
O(4)	0.5434 (10)	0.1546 (7)	0.4502 (5)	0.098 (3)
C(17)	0.2872 (17)	0.2888 (12)	0.4870 (9)	0.133 (7)
C(18)	0.2165 (16)	0.0255 (11)	0.4004 (8)	0.117 (6)

of S(1) and S(2) atoms in the π -conjugation *via* the central C(1)··C(2)··C(3)··C(4) moiety. The N(1) atoms contribute more clearly to this π -conjugation through the N(1)—C(1) bonds of 1.34(1)–1.358(5) Å, which are essentially shorter than the N(1)—C(5) bonds of 1.398(5)–1.41(1) Å. The difference between the N(2)—C(12) and N(2)—C(11) bond lengths at N(2) of the imidazole moieties [1.362(7)–1.37(1) and 1.404(7)–1.42(1) Å, respectively] is smaller than the difference between N—C bonds at the N(1) atom. The lengths of

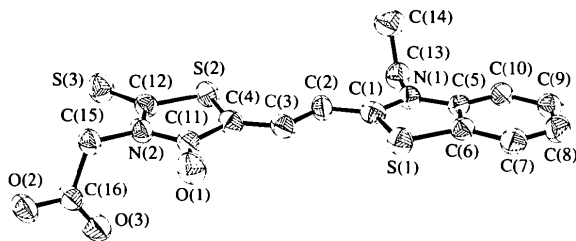


Fig. 2. Molecular structure and atomic numbering of the anion in (2). Displacement ellipsoids as in Fig. 1.

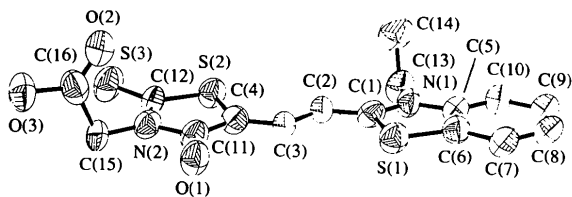


Fig. 1. Molecular structure and atomic numbering of 2-(3-ethyl-2-benzothiazolidene)rhodanine *N*-acetic acid in (1). The displacement ellipsoids are drawn at the 50% probability level.

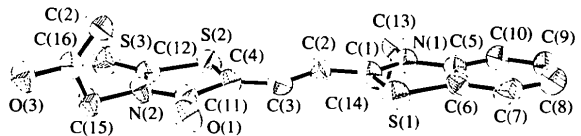


Fig. 3. Molecular structure and atomic numbering of the anion in (3). Displacement ellipsoids as in Fig. 1.

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for (2)
$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	U_{eq}
S(1)	0.2615 (2)	0.3124 (1)	0.9726 (1)	0.047 (1)
S(2)	0.1651 (2)	0.8558 (1)	0.9310 (1)	0.046 (1)
S(3)	0.0729 (3)	1.1043 (2)	0.8445 (1)	0.062 (1)
O(1)	0.1106 (6)	0.6676 (4)	0.7460 (2)	0.057 (2)
O(2)	0.0978 (5)	0.9598 (4)	0.5673 (2)	0.056 (2)
O(3)	0.3369 (6)	0.8867 (4)	0.6456 (2)	0.068 (2)
N(1)	0.3248 (6)	0.4078 (4)	1.1047 (2)	0.040 (2)
N(2)	0.0866 (6)	0.8751 (4)	0.7825 (2)	0.040 (2)
C(1)	0.2772 (7)	0.4431 (5)	1.0277 (3)	0.040 (2)
C(2)	0.2448 (7)	0.5660 (5)	0.9970 (3)	0.045 (2)
C(3)	0.2012 (7)	0.5954 (5)	0.9167 (3)	0.044 (2)
C(4)	0.1652 (8)	0.7169 (5)	0.8813 (3)	0.042 (2)
C(5)	0.3470 (7)	0.2772 (5)	1.1226 (3)	0.037 (2)
C(6)	0.3152 (7)	0.2120 (5)	1.0562 (3)	0.039 (2)
C(7)	0.3312 (8)	0.0808 (5)	1.0618 (3)	0.047 (2)
C(8)	0.3804 (8)	0.0188 (5)	1.1336 (4)	0.055 (2)
C(9)	0.4152 (8)	0.0854 (5)	1.1997 (3)	0.050 (2)
C(10)	0.3971 (8)	0.2142 (5)	1.1956 (3)	0.045 (2)
C(11)	0.1212 (8)	0.7432 (5)	0.7984 (3)	0.041 (2)
C(12)	0.1061 (7)	0.9483 (5)	0.8454 (3)	0.041 (2)
C(13)	0.3484 (8)	0.4990 (5)	1.1642 (3)	0.049 (2)
C(14)	0.1622 (9)	0.5606 (6)	1.2081 (4)	0.069 (3)
C(15)	0.0183 (8)	0.9276 (5)	0.7048 (3)	0.044 (2)
C(16)	0.1680 (8)	0.9226 (5)	0.6347 (3)	0.046 (2)
Li	0.1733 (14)	0.9866 (10)	0.4550 (6)	0.056 (4)
O(4)	0.6721 (8)	0.1515 (5)	0.6111 (3)	0.087 (2)
N(3)	0.3684 (9)	0.2485 (5)	0.6473 (3)	0.076 (3)
C(17)	0.4983 (12)	0.1743 (7)	0.6018 (4)	0.079 (3)
C(18)	0.1692 (12)	0.2687 (8)	0.6317 (5)	0.097 (4)
C(19)	0.4144 (14)	0.3125 (9)	0.7189 (5)	0.139 (6)
O(5)*	0.7865 (31)	0.4640 (30)	0.5257 (12)	0.165 (11)
N(4)*	1/2	1/2	1/2	0.072 (10)
C(20)*	0.4130 (126)	0.4592 (39)	0.4599 (28)	0.206 (37)
C(21)*	0.6799 (130)	0.4345 (50)	0.4938 (25)	0.209 (35)
C(22)*	0.5445 (53)	0.3999 (23)	0.4212 (21)	0.172 (17)
O(6)	0.3078 (6)	1.1214 (4)	0.4301 (2)	0.067 (2)
O(7)	0.0778 (10)	1.3531 (5)	0.3941 (4)	0.125 (3)

* O(5), N(4), C(20), C(21) and C(22) atoms of the dimethylformamide molecule, disordered around the inversion centre at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ [N(4) atom lies at this inversion centre], were refined with the assigned population parameters of $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ and $\frac{1}{2}$, respectively.

N—C sp^2 bonds in the imidazole molecule itself are also different: 1.349 and 1.370 \AA (Allen, Kennard, Watson, Brammer & Orpen, 1987). The very short N(1)—C(1) distances indicate the essentially multiple character of this bond, which agrees with the presence of partial positive charge on the N(1) atom of the benzimidazole moiety (see *e.g.* Bai, Chang & Xu, 1983). The bonds S(3)=C(12) [1.661 (9)—1.644 (6) \AA] and O(1)=C(11) [1.23 (1)—1.227 (7) \AA] have localized double-bond character, *cf.* the length of the S=C bond of 1.671 \AA in $(X)_2$ —C=S ($X = C, N, O, S$) and the length of the O=C bond of 1.208 \AA in cyclopentanones (Allen, Kennard, Watson, Brammer & Orpen, 1987).

3.2. Crystal packing

The molecules in crystal (1) are arranged in stacks extended along the a axis with somewhat alternating intrastack separations of $d = 3.41$ and 3.46 \AA [around the inversion centre (0,0,0) and $(\frac{1}{2}, 0, 0)$ respectively], see

Table 4. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for (3)
$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	U_{eq}
S(1)	0.3629 (1)	-0.4728 (2)	0.2499 (1)	0.050 (1)
S(2)	0.3076 (1)	0.1210 (2)	0.0055 (1)	0.049 (1)
S(3)	0.3040 (1)	0.4821 (2)	-0.0898 (1)	0.066 (1)
O(1)	0.3917 (1)	0.1860 (4)	0.1411 (2)	0.056 (1)
O(2)	0.3991 (1)	0.2708 (5)	-0.0353 (2)	0.053 (1)
O(3)	0.4174 (1)	0.5677 (4)	-0.0085 (2)	0.051 (1)
N(1)	0.3064 (1)	-0.5467 (5)	0.1692 (2)	0.040 (1)
N(2)	0.3538 (1)	0.3398 (5)	0.0332 (2)	0.042 (1)
C(1)	0.3281 (1)	-0.4127 (6)	0.1729 (3)	0.040 (2)
C(2)	0.3232 (1)	-0.2505 (6)	0.1234 (3)	0.043 (2)
C(3)	0.3456 (1)	-0.1145 (6)	0.1300 (3)	0.044 (2)
C(4)	0.3418 (1)	0.0486 (6)	0.0830 (3)	0.041 (2)
C(5)	0.3166 (1)	-0.7006 (6)	0.2252 (3)	0.040 (2)
C(6)	0.3478 (1)	-0.6847 (6)	0.2735 (3)	0.042 (2)
C(7)	0.3625 (1)	-0.8256 (7)	0.3307 (3)	0.055 (2)
C(8)	0.3458 (1)	-0.9815 (7)	0.3407 (3)	0.057 (2)
C(9)	0.3147 (1)	-0.9958 (7)	0.2939 (3)	0.053 (2)
C(10)	0.2999 (1)	-0.8564 (7)	0.2362 (3)	0.048 (2)
C(11)	0.3650 (1)	0.1890 (6)	0.0913 (3)	0.044 (2)
C(12)	0.3236 (1)	0.3286 (6)	-0.0168 (3)	0.044 (2)
C(13)	0.2739 (1)	-0.5228 (7)	0.1155 (3)	0.046 (2)
C(14)	0.2573 (1)	-0.3924 (9)	0.1574 (3)	0.075 (2)
C(15)	0.3741 (1)	0.4945 (7)	0.0280 (3)	0.047 (2)
C(16)	0.3988 (1)	0.4362 (6)	-0.0082 (3)	0.041 (2)
Na	-0.0041 (1)	0.2548 (2)	0.4940 (1)	0.045 (1)
O(4)	0.0178 (1)	-0.0002 (5)	0.4298 (2)	0.050 (1)
O(5)	0.0489 (1)	0.2569 (5)	0.5968 (2)	0.054 (1)
O(6)	-0.0561 (1)	0.3362 (5)	0.3967 (2)	0.054 (1)
O(7)	0.0131 (1)	0.4935 (5)	0.4176 (2)	0.050 (1)
O(8)	0.0738 (1)	0.4159 (6)	0.4306 (3)	0.065 (2)
O(9)	0.0	0.3505 (8)	3/4	0.061 (2)
O(10)	0.0545 (1)	0.1490 (6)	0.7634 (3)	0.069 (2)
O(11)	0.0	0.1203 (9)	1/4	0.067 (2)
O(12)	0.0596 (1)	0.2477 (6)	0.2686 (3)	0.082 (2)

Figs. 4 and 5. The neighbouring molecules within one stack are oriented in an antiparallel manner (head-to-tail) with the benzothiazole and 3-methylrhodanin-4-one moieties alternated along the axis of the stack. The character of molecular association observed in crystal (1) corresponds to the H aggregation of chromophores leading to a hypsochromic shift in the absorption spectrum of the crystal in relation to the spectrum of the dilute liquid (see *e.g.* Okuyama, 1993).

Only the S atoms form intermolecular contacts in crystal (1) which are shorter than the sums of the van der Waals radii of the corresponding atoms (Bondi, 1964), Table 6. Molecules (1) within one stack are related by the shortened contacts S(1)··S(1) of 3.755 (5) and S(1)··S(2) of 3.850 (4) \AA . The contacts S(1)··S(3) of 3.860 (5), S(2)··S(2) of 3.514 (6) [the shortest S··S contact in crystal (1)] and S(2)··S(3) of 4.095 (5) \AA are connecting the molecules of neighbouring stacks into the layers parallel to the ab plane of crystal (1). The molecules of the solvate dimethylsulfoxide are located between the layers, forming strong hydrogen bonds O(4)··H(3)—O(3) with the carboxyl groups of molecules (1) at the O(3)··O(4) distances of 2.580 (9) \AA . The dimethylsulfoxide molecules are connected head-to-tail by the shortened S(4)··S(4) contacts of 3.841 (8) \AA into the pairs around the inversion centres at $(\frac{1}{2}, 0, \frac{1}{2})$.

Table 5. Bond distances (Å) and angles (°) in molecule (1) and anions (2) and (3)

	(1)	(2)	(3)
S(1)—C(1)	1.75 (1)	1.735 (6)	1.742 (4)
S(1)—C(6)	1.734 (9)	1.728 (5)	1.740 (5)
S(2)—C(4)	1.75 (1)	1.733 (6)	1.749 (4)
S(2)—C(12)	1.724 (9)	1.717 (5)	1.727 (5)
S(3)—C(12)	1.661 (9)	1.644 (6)	1.646 (4)
O(1)—C(11)	1.23 (1)	1.227 (7)	1.235 (5)
O(2)—C(16)	1.19 (1)	1.269 (6)	1.245 (6)
O(3)—C(16)	1.33 (1)	1.224 (7)	1.262 (5)
N(1)—C(1)	1.34 (1)	1.356 (6)	1.358 (5)
N(1)—C(5)	1.41 (1)	1.402 (6)	1.398 (5)
N(1)—C(13)	1.48 (1)	1.461 (7)	1.481 (5)
N(2)—C(11)	1.42 (1)	1.404 (7)	1.407 (5)
N(2)—C(12)	1.37 (1)	1.362 (7)	1.369 (5)
N(2)—C(15)	1.45 (1)	1.455 (5)	1.454 (6)
C(1)—C(2)	1.40 (1)	1.374 (7)	1.375 (6)
C(2)—C(3)	1.38 (1)	1.390 (7)	1.385 (6)
C(3)—C(4)	1.37 (1)	1.389 (7)	1.361 (6)
C(5)—C(6)	1.38 (1)	1.384 (7)	1.399 (5)
C(6)—C(7)	1.41 (1)	1.392 (7)	1.381 (6)
C(7)—C(8)	1.37 (2)	1.367 (8)	1.378 (7)
C(8)—C(9)	1.37 (2)	1.395 (9)	1.390 (6)
C(9)—C(10)	1.39 (2)	1.364 (8)	1.380 (6)
C(10)—C(5)	1.38 (1)	1.387 (7)	1.384 (6)
C(4)—C(11)	1.42 (1)	1.428 (7)	1.428 (6)
C(13)—C(14)	1.51 (1)	1.503 (8)	1.502 (8)
C(15)—C(16)	1.51 (1)	1.509 (7)	1.512 (7)
C(1)—S(1)—C(6)	90.9 (4)	91.2 (2)	91.6 (2)
C(4)—S(2)—C(12)	92.1 (4)	92.3 (3)	93.1 (2)
C(1)—N(1)—C(5)	114.9 (8)	114.6 (4)	115.0 (3)
C(1)—N(1)—C(13)	122.8 (7)	122.5 (4)	122.3 (3)
C(5)—N(1)—C(13)	122.4 (7)	122.9 (4)	122.5 (4)
C(11)—N(2)—C(12)	115.3 (7)	116.1 (4)	116.1 (4)
C(11)—N(2)—C(15)	122.1 (8)	120.3 (4)	120.2 (3)
C(12)—N(2)—C(15)	122.3 (7)	123.4 (4)	123.7 (3)
S(1)—C(1)—C(2)	121.8 (7)	124.2 (4)	124.4 (3)
N(1)—C(1)—C(2)	127.2 (8)	124.8 (5)	125.0 (3)
C(1)—C(2)—C(3)	122.9 (9)	121.9 (5)	123.5 (3)
C(2)—C(3)—C(4)	127.6 (9)	125.4 (5)	125.5 (3)
C(3)—C(4)—S(2)	124.8 (7)	125.4 (4)	125.3 (3)
C(3)—C(4)—C(11)	124.1 (9)	123.8 (5)	125.0 (3)
S(1)—C(1)—N(1)	111.0 (6)	111.0 (4)	110.7 (3)
N(1)—C(5)—C(6)	111.3 (8)	111.5 (4)	111.9 (4)
C(5)—C(6)—S(1)	111.8 (7)	111.8 (4)	110.7 (3)
C(5)—C(6)—C(7)	120.5 (8)	120.2 (5)	120.8 (4)
C(6)—C(7)—C(8)	117 (1)	118.5 (5)	118.9 (4)
C(7)—C(8)—C(9)	122 (1)	120.7 (5)	120.3 (4)
C(8)—C(9)—C(10)	121 (1)	121.5 (5)	121.2 (5)
C(9)—C(10)—C(5)	117 (1)	117.8 (5)	118.7 (4)
C(10)—C(5)—C(6)	122.0 (9)	121.4 (5)	120.1 (4)
S(1)—C(6)—C(7)	127.7 (8)	128.0 (4)	128.4 (3)
C(10)—C(5)—N(1)	126.7 (9)	127.2 (5)	128.0 (3)
S(2)—C(4)—C(11)	111.1 (6)	111.1 (4)	109.7 (3)
C(4)—C(11)—N(2)	110.2 (8)	109.7 (5)	111.1 (3)
N(2)—C(12)—S(2)	111.2 (6)	110.8 (4)	110.0 (3)
O(1)—C(11)—N(2)	119.8 (8)	122.0 (5)	121.8 (4)
O(1)—C(11)—C(4)	130.0 (8)	128.3 (5)	127.1 (4)
S(2)—C(12)—S(3)	123.5 (6)	122.5 (3)	122.5 (3)
N(2)—C(12)—S(3)	125.2 (7)	126.7 (4)	127.4 (4)
N(1)—C(13)—C(14)	110.8 (8)	111.7 (5)	111.2 (4)
N(2)—C(15)—C(16)	111.4 (7)	115.8 (4)	114.2 (4)
O(2)—C(16)—O(3)	125.0 (8)	126.3 (5)	126.0 (4)
O(2)—C(16)—C(15)	124.8 (8)	112.6 (5)	119.8 (4)
O(3)—C(16)—C(15)	110.2 (9)	121.0 (5)	114.3 (4)

In an analysis of the crystal structure of organic charge-transfer complexes or organic conductors, the interaction (orbital overlap) between neighbouring molecules is estimated by a comparison of the intermolecular distances with the sum of the van der Waals radii of the contacting atoms. In molecular crystals at room temperature the orbital overlap is small if the inter-

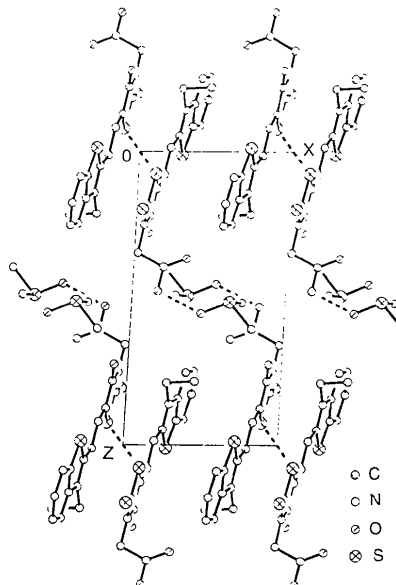


Fig. 4. Stacks along the *a* axis in crystal structure (1) (projection along the *b* axis). The hydrogen bonds O(3)—H...O(4) of 2.580(9) Å and the shortest intermolecular contacts S(2)...S(2) ($-x, 1-y, -z$) of 3.514(6) Å are marked by dotted lines.

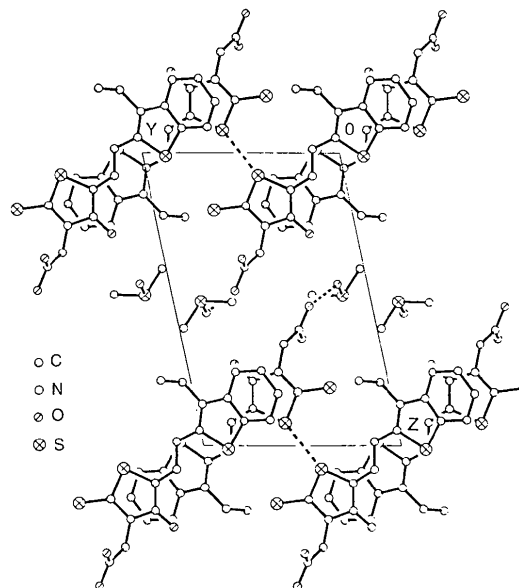


Fig. 5. Overlap of the molecules in the stacks in crystal structure (1) (projection along the *a* axis). The hydrogen bonds O(3)—H...O(4) and the shortest intermolecular contacts S(2)...S(2) ($-x, 1-y, -z$) are indicated by dotted lines.

Table 6. *The shortest intermolecular S...S contacts (Å) in crystals (1) and (2)**

Crystal (1)			
S(1)...S(1 ⁱ)	3.755 (5)	S(1)...S(2 ^{iv})	3.850 (4)
S(1)...S(3 ⁱⁱ)	3.860 (5)	S(2)...S(2 ^v)	3.514 (6)†
S(4)...S(4 ⁱⁱⁱ)	3.841 (8)		
Crystal (2)			
S(1)...S(3 ⁱⁱ)	3.682 (3)	S(2)...S(3 ⁱⁱⁱ)	3.938 (3)

Symmetry codes: (i) $1-x, -y, -z$; (ii) $x, y-1, z$; (iii) $1-x, -y, 1-z$; (iv) $-x, -y, -z$; (v) $-x, 1-y, -z$; (vi) $-x, 2-y, 2-z$. * The intermolecular S...S distances are given which are shorter than 4.0 Å. All the intermolecular S...S contacts in crystal (3) exceed 4.0 Å. † Shorter than twice the van der Waals radius of sulfur (3.60 Å; Bondi, 1964).

molecular distances are greater than the sum of the van der Waals radii. At distances smaller than this sum the contribution of orbital overlap increased exponentially. The intermolecular distances are necessary, but not sufficient criteria in the consideration of intermolecular charge-transfer interactions. In addition to the intermolecular distances it is also necessary to take into account the relative orientation of the orbitals of the molecules in contact when determining the orbital overlap (Shklover, Nagapetyan & Struchkov, 1990), the type of orbital interaction (e.g. bonding, non-bonding and antibonding) and the electron filling.

The 5-[2-(3-ethyl-2-benzothiazolidene)]rhodanine *N*-acetate anions in crystal (2) are also arranged in stacks along the *a* axis, with the antiparallel head-to-tail orientation of neighbouring anions within the stacks, in this way giving rise to the H aggregation of dye anions in crystal (2) (Fig. 6). The interplanar distances within the stacks alternate, they are 3.45 Å between the anions connected by the inversion centre at $(0\frac{1}{2}, 1)$ and 3.38 Å between the anions connected by the inversion centre $(\frac{1}{2}, \frac{1}{2}, 1)$. The overlaps of the dye molecules in crystal (1) and the dye anions in crystal (2) are similar. The stacks form the anionic layers parallel to the *ab* plane of crystal (2). Within the anionic layers, there are two intermolecular C...C contacts which are slightly shorter than the doubled van der Waals radius of the C atom: C(3)...C(13) 3.370(8) (within the stack) and C(7)...C(7) 3.270 Å (between the stacks).

The Li⁺ cations and the solvent molecules of dimethylformamide and water form the 'cationic' layers alternating with the anionic layers along the *c* direction. Every water molecule participates in two hydrogen bonds, two within the cationic layer [O(6)—H...O(7) ($1-x, y, z$) = 2.746(7) and O(7)—H...O(5) ($1-x, 2-y, 1-z$) = 2.81(3) Å] and two between the anionic and cationic layers [O(6)—H...O(3) ($1-x, 2-y, 1-z$) = 2.750(6) and O(7)—H...O(1) ($-x, 2-y, 1-z$) = 2.815(8) Å]. One molecule of dimethylformamide participates in the coordination of

the Li⁺ cations [Li—O(4)] and the second (disordered) serves as an acceptor in hydrogen bonding to an H₂O molecule [O(7)—H...O(5)].

The Li⁺ cations in crystal (2) have a very distorted tetrahedral surrounding of four O atoms, two O(2) atoms from two acetate groups, one O(4) atom of the dimethylformamide solvate and one O(6) atom of the H₂O molecule. The O—Li—O bond angles vary from 89.2(4) to 121.6(5)°. The Li—O distances are in the range 1.91(1)–1.98(1) Å. This is very close to the sum 1.97 Å of the crystal radii of O²⁻ (coordination number 2) and of Li⁺ [coordination number 4 (Shannon, 1976)]. The Li tetrahedra are edge-shared *via* the bridging atoms O(2) and O(2) ($-x, 2-y, 1-z$) into the dimers around the inversion centre $(0, 0, \frac{1}{2})$ at the Li...Li separation of 2.77(2) Å. A similar geometry has been found in the distorted tetrahedra [Li(H₂O)₄]⁺ in the crystal structure of diethyldithiocarbamate trihydrate Li(C₅H₁₀NS₂)₃·3H₂O [Li—O 1.895–2.049(3) Å, O—Li—O 96.6–118.8(2)° (Ymen, 1984)], which are also edge-sharing dimers. The fourfold coordination by O atoms and the Li—O and Li...Li distances observed in (2) are normal for small Li_{*n*} clusters with oxygen ligands (see e.g. Bidell, Shklover & Berke, 1991). The Li...Li separations may vary depending on the ligands from 2.20 to 2.75 Å, when the Li⁺ ions are participating in the multicentre bonds.

The head-to-tail orientation of neighbouring molecules and alternating intrastack separations of the flat molecules along the short *a* axis also occurs in crystal (4)

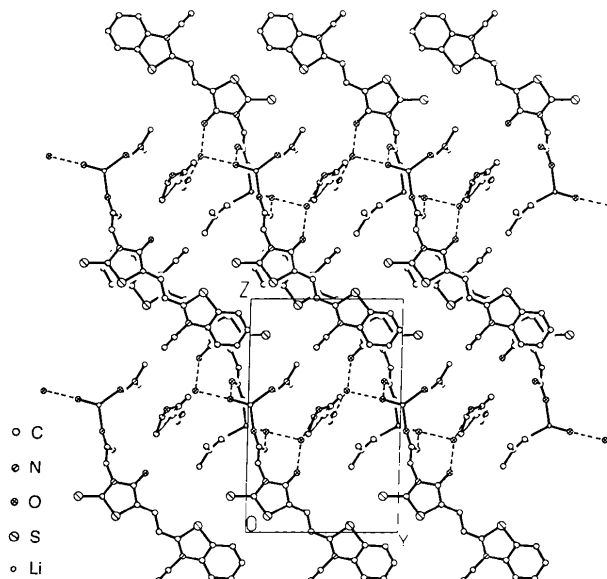


Fig. 6. Overlap of anions in (2) (projection along the *a* axis). The hydrogen bonds within the cation layer [O(6)—H...O(7) 2.746(7) and O(7)—H...O(5) 2.81(3) Å] and between cationic and anionic layers [O(6)—H...O(3) 2.750(6) Å and O(7)—H...O(1) 2.815(8) Å] are shown by dotted lines. The disordered molecule of crystallization, dimethylformamide, occupies a cavity at the inversion centre $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$.

[$a = 7.458(8) \text{ \AA}$]. The stacks also form sheets parallel to the ab plane. The sheets and (especially) the stack structure in crystals (1), (2) and (4) with the translation of 7.2–7.6 Å along the stack may be seen as a characteristic of the H aggregation of merocyanine dye molecules with head-to-tail orientation of neighbouring molecules within the stacks and with alternating intrastack separations.

The crystal structure of (3) is the first X-ray single crystal study of the J aggregation in a merocyanine dye crystal. The J aggregation of chromophores leads to a bathochromic shift in the absorption spectrum (see *e.g.* Okuyama, 1993). The anions are packed head-to-head into stacks which in turn are arranged into the layers (Fig. 7). The layers form the 'organic' bilayers parallel to the bc plane with van der Waals interactions within the bilayers and with the acetate groups oriented towards the outside of the bilayers. The ionic $\text{Na}^+ \cdots \text{O}$ interactions and hydrogen bonds $\text{O}—\text{H} \cdots \text{O}$ form the 'inorganic' layers between the organic bilayers.

In principle, the organic part of crystal (3) may be considered as a cumulated bilayered structure, one of two possible structures, formed by layers with two inseparable sides with hydrophilic and hydrophobic surfaces (Miyata & Miki, 1993), but with inorganic layers between the outer hydrophilic sides of the cumulated layers.

The infinite chains of Na octahedra may be distinguished in the inorganic layer of crystal (3), Fig. 8. Every Na^+ cation is coordinated by six water molecules at the $\text{Na}—\text{O}$ distances 2.389–2.476(4) Å, which are close to the sum 2.40 Å of the crystal radii of O^{2-} (coordination number 4) and Na^+ [coordination number 6 (Shannon, 1976)]. The hexa-coordination of Na^+ and the $\text{Na}—\text{O}$ separations found in (3) are typical for ionic organic

crystals (Dubchak, Shklover, Levitsky, Zhdanov & Struchkov, 1980). The distorted octahedra around the Na^+ ions in crystal (3) are edge-sharing *via* two pairs of water O atoms, O(4), O(4) and O(7), O(7). They form extended chains along the b direction with $\text{Na} \cdots \text{Na}$ separations of 3.454(4) and 3.588(4) Å. The mean $\text{Na}—\text{O}$ distance in the structures with octahedrally surrounded Na^+ equals 2.43 Å (ionic radius of Na^+ is 1.05 Å; Shannon, 1976).

The 16 'active' H atoms of nine symmetrically independent water molecules in (3) participate in the formation of hydrogen bonds (Table 7). There are 11 hydrogen bonds within the inorganic layer and five (one of them bifurcated) are between the inorganic and organic bilayers. The hydrogen bonds of the water O(8) atom are of special interest. This molecule participates in the formation of hydrogen bonds within the inorganic layer [O(8) \cdots H(72)—O(7) (x, y, z) and O(8) \cdots H(121)—O(12) (x, y, z)] as the acceptor and in two hydrogen bonds (one of them bifurcated) between the inorganic layer and the organic bilayer as the donor [O(8)—H(81) \cdots O(3) ($\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$) and O(8)—H(82) \cdots O(1) ($\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$), O(8)—H(82) \cdots O(2) ($\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$)].

Every water oxygen in crystal (3) has tetra-coordination formed either by two $\text{Na}—\text{O}$ bonds and two hydrogen bonds [atoms O(4) and O(7)], one $\text{Na}—\text{O}$ bond and three hydrogen bonds [atoms O(5) and O(6)] or four hydrogen bonds [atoms O(8), O(9), O(10), O(11) and O(12)].

The O atoms of the anion bilayers do not participate in the coordination of the Na^+ cations, whose oxygen surrounding is formed exclusively by water oxygens. Conventionally the organic bilayers in crystal (3) can be considered as negatively charged and the inorganic layers as positively charged.

The single crystal data on the structure of inorganic layered supports may be used for the selection of simple molecular lattices for subsequent surface-structure calculations with the aim of elucidating surface reconstruction.

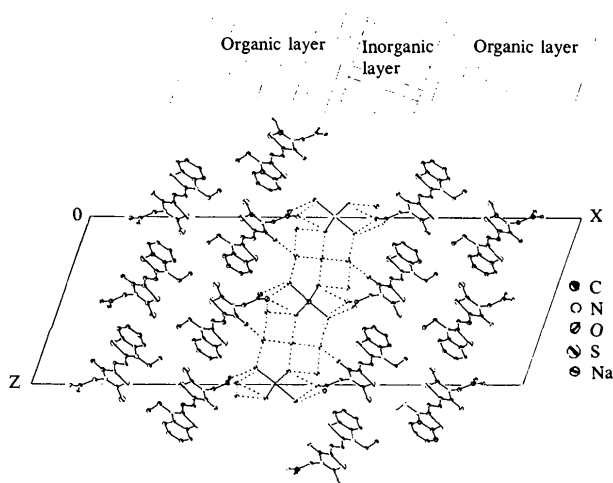


Fig. 7. The ac projection of (3). The inorganic layer containing the Na^+ cations and the water molecules are situated between cumulated organic bilayers formed by the stacks of anions (J aggregates). The O atoms of the anions are oriented towards the outer surfaces of the organic bilayer, but do not participate in the interaction with the Na^+ ions.

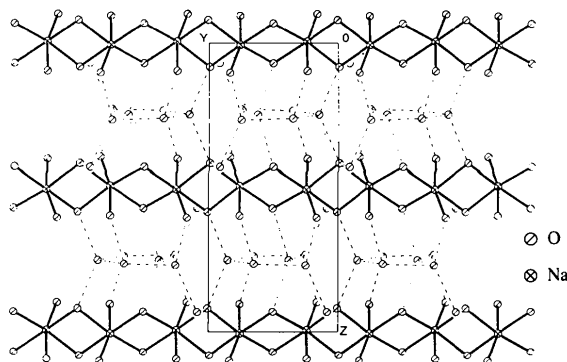


Fig. 8. Structure of the inorganic layer in the crystal of (3) (the bc projection). The hydrogen bonds are shown by dotted lines. The distorted octahedra around the Na^+ ions are edge-sharing *via* two pairs of water O atoms forming chains extended along the b axis.

Table 7. Hydrogen bonds $A-H \cdots B$ in crystal (3)

$A-H \cdots B$	$A \cdots B$ (Å)	$A-H$ (Å)	$H \cdots B$ (Å)	$A-H \cdots B$ (°)
Within the inorganic layer				
O(4)—H(42) \cdots O(11)	2.940 (6)	0.80 (5)	2.15 (4)	173 (4)
O(5)—H(51) \cdots O(3 ⁱ)	2.801 (5)	0.95 (5)	1.85 (5)	175 (3)
O(5)—H(52) \cdots O(10)	2.791 (6)	0.75 (5)	2.04 (5)	175 (5)
O(6)—H(62) \cdots O(5 ⁱⁱ)	2.868 (4)	0.72 (5)	2.14 (5)	176 (5)
O(7)—H(72) \cdots O(8)	2.793 (5)	0.77 (5)	2.02 (5)	177 (5)
O(7)—H(71) \cdots O(9 ⁱⁱⁱ)	2.857 (5)	0.82 (5)	2.04 (5)	172 (4)
O(9)—H(91) \cdots O(1)	2.832 (5)	0.74 (5)	2.11 (5)	167 (5)
O(10)—H(102) \cdots O(12 ⁱⁱⁱⁱ)	2.787 (6)	0.78 (5)	2.01 (5)	175 (5)
O(11)—H(111) \cdots O(12)	2.811 (6)	0.79 (5)	2.09 (5)	151 (4)
O(12)—H(122) \cdots O(6 ^v)	2.763 (6)	0.91 (5)	1.88 (5)	164 (4)
O(12)—H(121) \cdots O(8 ^v)	2.804 (6)	0.82 (5)	2.00 (5)	166 (5)
Between the inorganic layer and organic bilayer				
O(4)—H(41) \cdots O(3 ⁱ)	2.878 (6)	0.72 (5)	2.19 (4)	161 (5)
O(6)—H(61) \cdots O(2 ⁱⁱ)	2.767 (6)	1.08 (5)	1.69 (5)	176 (2)
O(8)—H(82) \cdots O(1 ⁱⁱⁱ)	2.965 (6)	0.70 (5)	2.46 (6)	131 (5)
O(8)—H(82) \cdots O(2 ⁱⁱⁱⁱ)	3.052 (5)	0.70 (5)	2.48 (5)	142 (6)
O(8)—H(81) \cdots O(3 ⁱ)	2.727 (5)	0.84 (5)	1.91 (5)	166 (4)
O(10)—H(101) \cdots O(1 ^{viii})	2.719 (5)	0.66 (5)	2.06 (4)	170 (5)

Symmetry codes: (i) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (ii) $-x, 1 - y, 1 - z$; (iii) $x, -y, \frac{1}{2} + z$; (iv) $-x, y, \frac{1}{2} - z$; (v) x, y, z ; (vi) $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$; (vii) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (viii) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$.

This may be performed *via* the symmetry lowering when going from the crystal to the surface translations (Harrison, 1989), although care has to be taken because surface reconstructions may also occur without any surface coverage.

The anions in crystal (3) form stacks extended along the *b* axis (Figs. 7 and 9). All the interplanar separations between the anions within one stack are equal (3.389 Å) and do not alternate as in crystals (1) and (2). The structure of these uniform stacks corresponds to the definition of so-called J aggregates (Maskasky, 1991; Okuyama, 1993). In the stacks, the overlap of the five-membered S-containing heterocycles is essential. In spite of quite small interplanar separations, there are no interanionic distances in the J aggregates of crystal (3) shorter than the van der Waals distances; the shortest are close to the corresponding van der Waals separations (Bondi, 1964): N(2) \cdots C(1) 3.410 (6), C(4) \cdots C(5) 3.440 (7), C(2) \cdots C(9) 3.474 (7) and C(6) \cdots C(11) 3.485 (7) Å. The mean plane of the anion forms a dihedral angle of 105.9° with the inorganic layer (the *bc* plane of crystal 3). The long axis of the anion [approximately the line C(8) \cdots C(12)] forms an angle of 84.9° with the normal to the inorganic cation layer. The arrangement of the anions in crystal (3) may be characterized as a 'herringbone' structure.

The herringbone-type of arrangement is also found in other compounds, *e.g.* the mixed organic-inorganic crystals (5) built up of anions (Cr₂O₇)²⁻, (NO₃)⁻, (CuCl₄)²⁻, (COO)²⁻, (SO₄)²⁻, (HSO₄)_{*n*}⁻, (H₂PO₄)_{*n*}⁻ and (C₄H₅O₆)_{*n*}⁻ with 2-amino-5-nitropyridinium cations (Pecaut & Masse, 1993; Bagieu-Beucher, Masse & Tranqui, 1991; Masse & Zyss, 1991).

A layered structure is found, *e.g.* for the octahydrate of

trisodium *cis*-1,3,5-triphenylcyclotrisiloxan-1,3,5-triolate, Na₃[PhSi(O)O]₃³⁻·8H₂O (6), which is built up of doubled anionic layers having hydrophobic and hydrophilic surfaces (Dubchak, Shklover, Levitsky, Zhdanov & Struchkov, 1980). Here the Na⁺ cations and water molecules are situated between the hydrophilic surfaces of neighbouring layers. The three layered sheets are formed by hydrogen bonds Si—O—H \cdots O < [O \cdots O 2.644–2.929 (2) Å] and Na⁺ \cdots O interactions [2.298–2.529 (1) Å]. Pairs of sheets are packed through the hydrophobic surfaces in bilayers. By these means, crystal (6) is a mica-like hybrid of a siloxane and a silicate structure. The interaction of ion-dipole layers with the double anionic layers is presumably electrostatic. Crystal (6) seems to be very stable because it is often formed during catalytic interconversions of organosiloxanes. The known high tendency for close packing of triphenylsiloxane and the accommodational possibilities of non-directional ionic interactions within the hydrophilic interfaces may explain the stability of crystal (6). Another reason could be the direct ionic interaction of the atoms of anionic organic layers and inorganic cations, which is absent in crystal (3).

The direct coordinative bonding between layers of different chemical nature is not unusual and was observed in the light-green crystal of the sandwich-type nickel oxide complex [PhSiO]₆(μ₄-O)₄[Ni₈(μ₃-O)₂](μ₃-O)₄(μ₄-O)₂[PhSiO]₆ (7) (Levitsky *et al.*, 1991). The inner nickel oxide layer of complex (7) is identical to a fragment of the NiO crystal structure (sodium chloride type) parallel to the (111) plane. The outer cyclohexasiloxanolate ligands [PhSi(μ-O)O]₆ of complex (7) have approximate C₃ symmetry. The Ni—O distances in (7) [2.006–2.176 (9) Å] are close to 2.097 (1) Å in the NiO structure (Rooksby, 1948) and to other Ni compounds with octahedral coordination. The 12-membered siloxane rings retain the usual crown conformation. The closeness of the symmetry and the dimensions of the 'external' bonds of the siloxane and nickel oxide parts determine the stability of complex (7).

The *n*-nonylammonium tetraiodoplumbate(II) (8) (Nagapetyan *et al.*, 1988) has a layer structure and is composed of [PbI₄²⁻]₂ polyanion networks and C₉H₁₈NH₃⁺ cations oriented perpendicular to the polyanionic nets. In contrast to the PbI₂ crystal, where Pb and I atoms are in different planes, the Pb and I(1) atoms are

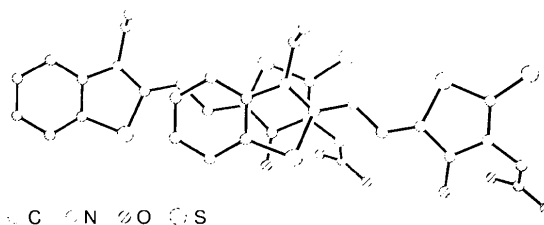


Fig. 9. Overlap of the anions within one of the stack in (3) (projection on the mean plane of the anion).

practically in the same plane in (8). The connection of polyhedra in (8) and PbI_2 also differs. Nevertheless, the band gap ΔE_g of (8) (2.4 eV at 293 K) is close to that observed for PbI_2 . The closeness of the surface of the ($a \times b$) area in crystal (8) (78.67 \AA^2) to the cross-section of four paraffin chains positioned above and below of this face in crystal (8) ($18.24 \times 4 = 72.96 \text{ \AA}^2$) and the observed direct ionic interactions of atoms of $\text{C}_9\text{H}_{18}\text{NH}_3^+$ cations with the anionic layers $[\text{PbI}_4^-]_2$ are factors which stabilize (8).

In conclusion, the crystal structure of (3) together with those of (5)–(8) show the tendency to form two-dimensional separate organic and inorganic motifs (layers) in the mixed structures, with intrinsic mutual structural dependence. The character of association of anions into the stacks (J aggregation) and stacks into the organic cumulated bilayers in the sodium salt (3) seems to be of general importance for the given class of merocyanine dyes. The principle difference of the layered organic-inorganic structure (3) from layered structures such as (5)–(8) is the possibility of significant change of important characteristics of one (organic) partial structure (shift of absorption band) by small variations of the other (inorganic) part.

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