

with K⁺ cations (Hodgson & Raymond, 1972). K—O distances [2.72 (2) Å for O(THF) and 2.68 (2) Å for O(dioxane)] are only slightly shorter than in this latter species [K—O(diglyme) 2.792 (5), 2.741 (4) Å]. The coordination geometry around each cation is approximately tetrahedral (see Table 4).

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Structures of Two Dibenzotetrathiafulvalene (DBTTF) Salts: (DBTTF)Cu(NCS)₂ and a Redetermination of (DBTTF)I₃

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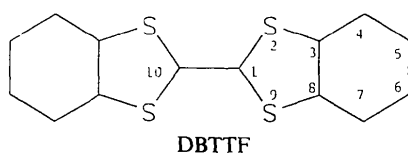
Abstract. 2,2'-Bi-1,3-benzodithiolylianium triiodide (1), C₁₄H₈S₄⁺.I₃⁻, *M_r* = 685.18, monoclinic, *C*2/*m*, *a* = 19.831 (4), *b* = 9.266 (1), *c* = 14.515 (3) Å, β = 90.03 (2)°, *V* = 2667.2 (8) Å³, *Z* = 6, *D_x* = 2.560 g cm⁻³, λ(Mo *K*α) = 0.71073 Å, μ = 56.62 cm⁻¹, *F*(000) = 1890, *T* = 295 K, *R* = 0.0434 for 2455 reflections. 2,2'-Bi-1,3-benzodithiolylianium bis(isothiocyanato)cuprate(I), (2), C₁₄H₈S₄⁺.Cu(NCS)₂⁻, *M_r* = 484.18, triclinic, *P* $\bar{1}$, *a* = 8.390 (5), *b* = 9.667 (6), *c* = 12.699 (7) Å, α = 95.07 (5), β = 108.25 (5), γ = 112.50 (4)°, *V* = 877.9 (8) Å³, *Z* = 2, *D_x* = 1.831 g cm⁻³, λ(Mo *K*α) = 0.71073 Å, μ = 19.35 cm⁻¹, *F*(000) = 486, *T* = 295 K, *R* = 0.142 for 1647 reflections. In compound (1) the DBTTF ions pack in superimposed triads with short S...S distances of 3.492 (6) Å. The triads are well separated along the triad axis by triiodide ions; however, adjacent triad stacks show S...S con-

tacts of 3.629 (6) Å. There are a number of S...I contacts shorter than the sum of the van der Waals radii, 3.654 (2) to 3.797 (2) Å. In compound (2) the DBTTF ions form infinite stacks with each member of the stack shifted by about a half a molecule from its two neighbors in the stack. The Cu(NCS)₂⁻ ions form two infinite two-dimensional sheets between the stacks along the long axes of the DBTTF ions preventing any interstack S...S interactions. The Cu(NCS)₂⁻ ions are slightly bent with a 3.055 (9) Å separation between S of one ion and Cu^I of another.

Introduction. There is considerable interest in conducting organic compounds which have highly anisotropic electrical, optical and magnetic properties, and the discovery of superconductivity in some of these systems has heightened this interest. The bis-(ethylenedithio)tetrathiafulvalene (BEDT-TTF) complexes have generated the most recent interest (Williams *et al.*, 1987) with (BEDT-TTF)₂Cu(NCS)₂

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exhibiting a T_c around 11 K (Urayama *et al.*, 1988). It is also significant to note that polycrystalline-pressed samples of β_p -(BEDT-TTF) $_2$ I $_3$ at ambient pressure are superconducting with a T_c of 7.5 K (Schweitzer, Gogu, Grimm, Kahlich & Keller, 1989); however, pressed polycrystalline (BEDT-TTF) $_2$ -Cu(NCS) $_2$ does not show bulk superconductivity. In an attempt to understand more fully the electrocrystallization process used to prepare many of these organic superconductors, we have been reinvestigating the electrochemistry of some aromatic hydrocarbons and other organosulfur analogues. Dibenzotetrathiofulvalene (DBTFF) has attracted considerable attention during the past decade and the structures and electrical conductivities of a number of DBTTF compounds have been reported (Grossel, Edwards, Hibbert & El Nol, 1989; Matsubayashi, Shimizu & Tanaka, 1987, and references therein). In our electrochemical investigations utilizing the two anions which produce the highest T_c superconductors in the BEDT-TTF series, we have prepared compounds of (DBTFF)I $_3$ and (DBTFF)-Cu(NCS) $_2$ which we would like to report. The structure of (DBTFF)I $_3$ has been reported previously (Shibaeva, Rozenberg, Aldoshina, Lyubovskaya & Khidekel, 1979); however, the use of Cu radiation and no absorption correction resulted in an R factor of 0.11. Unlike the BEDT-TTF series no mixed oxidation state compounds have been prepared; however, the chemical formula of the I $_3^-$ salt has been widely misquoted as (DBTTF) $_2$ I $_3$ (*e.g.* Tanaka, Honda, Katayama & Tanaka, 1985). Electrocrystallization does not produce good crystals of (DBTFF)-Cu(NCS) $_2$; however, the data are sufficient to describe the packing interactions.



Experimental. Crystals of (DBTFF)I $_3$ (1) and (DBTFF)Cu(NCS) $_2$ (2) were obtained by electrocrystallization. H cells were fitted with coarse frits and platinum electrodes (2.5 cm length by 0.1 cm diameter). 1,1,2-Trichloroethane, TCE, freshly distilled from P $_2$ O $_5$ was used as solvent. The anode and cathode compartments for compound (1) each contained 10 ml of a solution of 176 mg *n*-Bu $_4$ NI $_3$ in 20 ml of TCE. The anode compartment was saturated with DBTFF. The H cell was flushed with Ar, sealed and electrolyzed at a constant current of 1.80 μ A (0.75–0.86 V) for five days. The electrodes were washed with TCE and about 3 mg of weakly adhered, flat, black shiny crystals were scraped from the electrode. For compound (2), TCE was added to

76 mg of CuNCS, 60 mg KSCN and 165 mg 18-crown-6 to give a volume of 25 ml. 8 mg of DBTFF were dissolved in 5 ml of TCE and placed in the anode compartment along with 10 ml of the solvent mixture. The remainder of the solvent mixture was added to the cathode compartment. The sealed and purged cell was electrolyzed at 0.30, 0.50, 0.70, 1.10 and 2.20 μ A over a four-day period but no crystal growth was observed. When the current was raised to 3.00 μ A (2.39 V), crystals began to grow and after an additional five days 3.2 mg of black shiny microcrystals were harvested. The crystals adhered strongly to the electrodes and grew in clusters of flat, very thin platelets along the length of the electrode. One useable crystal was found; however, powder patterns of the microcrystals could be indexed from the single-crystal data. Repeated attempts to grow better single crystals have not been successful.

All X-ray data collected on a Nicolet R3m/ μ update of a P2 $_1$ diffractometer; $\sum w(|F_o| - |F_c|)^2$ refined with $w = [\sigma^2(F_o) + 0.00027F_o^2]^{-1}$. All computer programs supplied by Nicolet for Desktop 30 Microclipse and Nova 4/c configuration (Nicolet Instrument Corporation, 1986); atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Compound (1). A black crystal of dimensions 0.32 \times 0.28 \times 0.15 mm was used to collect data in the ω mode ($3 \leq 2\theta \leq 55^\circ$), variable scan rate of 4 to 29.3° min $^{-1}$ using graphite-monochromated Mo $K\alpha$ radiation; lattice parameters from a least-squares refinement of 25 reflections ($23.3 \leq 2\theta \leq 28.86^\circ$), systematic absences (hkl , $h + k = 2n + 1$) and unit-cell dimensions were consistent with monoclinic space group $C2/m$ and several orthorhombic space groups, axial photographs and a careful comparison of $\bar{h}kl$ and hkl intensities indicated monoclinic symmetry; monitored reflections (374 and 461) showed maximum random deviations of $\pm 2\%$; 3252 independent reflections measured ($h = -25, 25$; $k = 0, 12$; $l = 0, 10$) ($R_{\text{merge}} = 0.013$); 2455 had $I \geq 3\sigma(I)$; Lorentz-polarization corrections and ψ -scan-based empirical absorption correction (transmission factors 0.132–0.070) applied; structure solved by direct methods; there are two independent triiodide ions in the unit cell with all iodine atoms lying in planes at $y = 0$ and $\frac{1}{2}$. One triiodide lies in a general position in the mirror plane while the other is at a $2/m$ center; there are two independent DBTTF molecules per cell, one lies at a $2/m$ center, atoms C(11) to C(16), while the other contains the mirror plane, atoms C(1) to C(10).

H atoms found in difference map and refined with isotropic thermal parameters; $R = 0.0434$, $wR = 0.0447$ for 180 parameters and 2455 reflections ($R = 0.0592$ and $wR = 0.0466$ for all 3252 observed

independent reflections), $S = 1.431$, $(\Delta/\sigma)_{\max} = 0.011$; largest peaks in the final difference map of -1.07 and $0.93 \text{ e } \text{Å}^{-3}$ located near I atoms; isotropic extinction correction $F = F_c/[1.0 + 0.002x F_c^2/\sin(2\theta)]^{0.25}$ where x refined to 0.00033 (2). Table 1 is a list of atomic positional parameters, while Table 3 gives selected distances and angles and Fig. 1 presents a packing diagram. The structure is consistent with that reported by Shibaeva, Rozenberg, Aldoshina, Lyubovskaya & Khidekel (1979); space group $B2/m$, $a = 19.888$ (4), $b = 14.551$ (2), $c = 9.294$ (1) Å, $\beta = 90.03$ (3)°.

Compound (2). A very thin black crystal of dimensions $0.38 \times 0.38 \times 0.02$ mm was used to collect data in the ω mode ($3 \leq 2\theta \leq 50^\circ$), variable scan rate of 4 to $29.3^\circ \text{ min}^{-1}$ using graphite-monochromated Mo $K\alpha$ radiation; lattice parameters from a least-squares refinement of 25 reflections ($21.15 \leq 2\theta \leq 29.81^\circ$), no systematic absences consistent with space group $P\bar{1}$; monitored reflection (102) showed a $\pm 4\%$ random variation in intensity; a very poor data set with 3294 reflections collected, 3069 independent ($R_{\text{merge}} = 0.01$), 1647 had $I \geq 3\sigma(I)$; Lorentz-polarization corrections and ψ -scan-based empirical absorption correction (transmission factors 0.527–0.930) applied; structure solved by direct methods, H atoms located in difference map but allowed to ride at a fixed distance from attached atom with refined isotropic thermal parameter; $R = 0.142$, $wR = 0.190$ for 226 parameters and 1647 reflections, $S = 0.906$, $(\Delta/\sigma)_{\max} = 0.008$; largest peaks in the final difference map of -1.76 and $2.53 \text{ e } \text{Å}^{-3}$; isotropic extinction correction with x refined to 0.0011 (1). Table 2 is a list of atomic positional parameters, while Table 3 gives selected distances and angles and Fig. 2 is a packing diagram of compound (2).*

Discussion. There are two independent molecules in compound (1). Molecule (1A) has a mirror plane passing through the length of the molecule and perpendicular to the molecular plane. Molecule (1B) lies on a site of $2/m$ symmetry. The (1B) molecules lie at each corner of the unit cell and at the center of the two faces with the (1A) molecules lying in sandwich fashion on either side. This arrangement leads to closely spaced DBTTF molecules occurring in triads. The molecules are superimposed and the S...S separation between DBTTF molecules within the triad is only 3.492 (6) Å which is considerably smaller than the sum of the van der Waals radii. The central molecule in the triad is planar while the outer two

Table 1. Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($\text{Å}^2 \times 10^3$) for compound (1)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
I(1)	3922 (1)	0	261 (1)	53 (1)
I(2)	4143 (1)	0	2239 (1)	63 (1)
I(3)	3704 (1)	0	-1715 (1)	63 (1)
I(4)	5000	0	5000	80 (1)
I(5)	3561 (1)	0	5462 (1)	103 (1)
C(1)	3297 (4)	5000	837 (5)	39 (2)
S(2)	3369 (1)	3422 (2)	1463 (1)	47 (1)
C(3)	3426 (3)	4237 (6)	2532 (4)	44 (2)
C(4)	3465 (3)	3494 (7)	3356 (4)	53 (2)
C(5)	3500 (3)	4249 (7)	4173 (4)	61 (2)
C(6)	3209 (3)	5000	-99 (5)	39 (2)
S(7)	3151 (1)	3422 (2)	-719 (1)	46 (1)
C(8)	3018 (2)	4255 (6)	-1781 (3)	39 (2)
C(9)	2914 (3)	3494 (6)	-2594 (4)	50 (2)
C(10)	2803 (3)	4267 (7)	-3392 (4)	58 (2)
C(11)	5045 (4)	5000	475 (5)	46 (3)
S(12)	5108 (1)	6579 (2)	1087 (1)	52 (1)
C(13)	5210 (3)	5762 (6)	2155 (4)	48 (2)
C(14)	5282 (3)	6525 (8)	2971 (4)	58 (2)
C(15)	5360 (3)	5738 (8)	3772 (4)	65 (2)

Table 2. Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($\text{Å}^2 \times 10^3$) for compound (2)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Cu	3472 (4)	-4606 (3)	5686 (3)	58 (1)
N	5654 (18)	-4058 (16)	6860 (16)	44 (6)
C	6843 (38)	-3617 (22)	7725 (23)	64 (13)
S	8552 (9)	-2935 (8)	8938 (6)	71 (3)
N'	1402 (26)	-5250 (19)	4404 (15)	48 (9)
C'	97 (29)	-5644 (19)	3602 (15)	48 (9)
S'	-1949 (7)	-6258 (6)	2596 (5)	46 (2)
C(1)	9291 (23)	465 (16)	16074 (13)	23 (7)
S(2)	9727 (6)	-762 (4)	16894 (4)	31 (2)
C(3)	11714 (18)	663 (18)	17969 (12)	19 (5)
C(4)	12725 (29)	366 (26)	18876 (22)	57 (11)
C(5)	14314 (26)	1562 (23)	19701 (15)	39 (9)
C(6)	14940 (32)	3039 (22)	19464 (21)	51 (10)
C(7)	13836 (27)	3376 (24)	18524 (15)	42 (9)
C(8)	12232 (23)	2118 (16)	17763 (15)	27 (7)
S(9)	10811 (7)	2359 (5)	16536 (4)	34 (2)
C(10)	7682 (23)	-56 (18)	15083 (16)	25 (7)
S(11)	7288 (6)	1181 (4)	14286 (4)	31 (2)
C(12)	5197 (27)	-199 (20)	13313 (17)	40 (9)
C(13)	4030 (29)	135 (23)	12343 (13)	39 (9)
C(14)	2363 (28)	-972 (21)	11662 (20)	43 (10)
C(15)	1843 (25)	-2521 (24)	11759 (19)	45 (10)
C(16)	2974 (23)	-2889 (18)	12631 (15)	28 (6)
C(17)	4590 (24)	-1678 (23)	13454 (19)	43 (9)
S(18)	6109 (6)	-1964 (5)	14600 (4)	33 (2)

are slightly bowed away from the central molecule. The (1A) molecules of one triad stack interact with the (1A) molecules of an adjacent stack with S...S distances of 3.629 (6) Å, e.g. S(2) and S(7) ($0.5-x$, $0.5-y$, $-z$). One independent I_3^- molecule lies on the mirror plane and the other lies on a site of $2/m$ symmetry. They form almost perpendicular arrays filling the voids within the triad stacks forming continuous I_3^- regions through the crystal via the voids.

* Lists of bond lengths and angles, H-atom coordinates, anisotropic thermal parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53174 (51 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Selected bond lengths (Å) and angles (°) for compounds (1) and (2)

The largest of either the average deviations or the standard deviations are given in parentheses. The bonds are identified in the scheme. All equivalent bonds are averaged.

	(1A)	(1B)	(2)
C(1)—S(2)	1.724 (4)	1.716 (4)	1.70 (2)
C(1)—C(10)	1.37 (1)	1.39 (2)	1.40 (2)
S(2)—C(3)	1.736 (7)	1.738 (6)	1.73 (2)
C(3)—C(4)	1.386 (8)	1.386 (8)	1.40 (4)
C(3)—C(8)	1.40 (2)	1.41 (1)	1.38 (2)
C(4)—C(5)	1.38 (1)	1.381 (9)	1.38 (4)
C(5)—C(6)	1.38 (2)	1.37 (1)	1.42 (3)
Cu—N			1.81 (1)
Cu—N'			1.81 (2)
N—C			1.14 (3)
N'—C'			1.14 (2)
C—S			1.61 (2)
C'—S'			1.63 (2)
I(1)—I(2)	2.905 (1)		
I(1)—I(3)	2.901 (1)		
I(4)—I(5)	2.932 (1)		
S(2)—C(1)—S(9)	116.0 (4)	117.0 (4)	118 (1)
S(2)—C(1)—C(10)	122.0 (2)	121.5 (2)	121 (1)
C(1)—S(2)—C(3)	95.9 (4)	95.7 (3)	94.5 (5)
S(2)—C(3)—C(8)	116.1 (2)	115.8 (2)	116 (3)
C(4)—C(3)—C(8)	120.2 (3)	120.7 (4)	121 (1)
C(3)—C(4)—C(5)	119.0 (7)	117.4 (6)	118 (2)
C(4)—C(5)—C(6)	120.9 (4)	121.9 (4)	120 (2)

The I(4)⋯I(2), I(5)⋯I(3) ($x, y, 1+z$), I(3)⋯I(2) ($1-x, -y, -z$) and I(1)⋯I(1) ($1-x, -y, -z$) distances of 4.351 (1), 4.107 (1), 4.337 (1) and 4.342 (1) Å are less than or within the range of reported van der Waals distances for iodine, 4.30 to 4.64 Å. There are a number of S⋯I contacts shorter than the sum of the van der Waals radii, e.g. S(7)⋯I(3) = 3.654 (2), S(2)⋯I(2) = 3.698 (2), S(2)⋯I(1) = 3.782 (2) and S(7)⋯I(1) = 3.797 (2) Å. The distance between S and the carbon of the connecting double bond averages 1.722 (6) Å while the distance between sulfur and the carbon of the benzene ring averages 1.737 (7) Å, which is consistent with literature average values of 1.724 (3) and 1.744 (7) Å for (DBTTF)₂Cu₂Br₆ (Honda, Katayama, Tanaka & Tanaka, 1985) and 1.719 (6) and 1.741 (7) Å for (DBTTF)(SnEt₂Cl₃) (Matsubayashi, Shimizu & Tanaka, 1987). The central C=C bond of 1.38 (1) Å is also consistent with the lengthening observed for the two reference compounds, 1.397 (6) and 1.37 (1) Å.

If there is a strong intra- and interstack interaction the electronic band formed from the highest occupied molecular orbitals should be completely filled leading to no unpaired electrons unless there is overlap with an empty band. If orbital overlap of the highest occupied molecular orbital is strong for the triad and weak or non-existent between triads, bonding, non-bonding and antibonding orbitals should result in an odd electron being in a non-bonding orbital. Weak coupling between independent triads might be observed at low temperatures. If there is no

overlap between the highest occupied molecular orbitals, each DBTTF ion would act as an independent cation radical with possible coupling between members within each triad. The EPR spectrum of a powder sample shows a very broad, weak spectrum with a linewidth of 2.65×10^{-2} T. A very small single crystal oriented approximately along the b axis gave a spectrum with a very weak but sharp central line (width 1.5×10^{-3} T) and possibly weak outer lines. Rotation of the sample has no effect on the central sharp line. The conductivity measured along the b axis is reported to be 0.05 S cm^{-1} (Shibaeva, Rozenberg, Aldoshina, Lyubovskaya & Khidekel, 1979).

(DBTTF)Cu(NCS)₂, compound (2), exhibits a different packing arrangement. The DBTTF molecules are arranged in stacks with alternating DBTTF molecules parallel and oriented in the same direction but shifted by almost a half of a molecular unit. One five-membered ring of each molecule in the stack overlaps with another above and below with the closest intrastack S⋯S distances of S(11)⋯S(2) ($4-x, -y, 3z$) = 3.421 (9) and S(18)⋯S(9) = 3.450 (9) Å shorter than the sum of the van der Waals radii. The stacks are separated by two-dimensional sheets of Cu(NCS)₂⁻ ions which prevent S⋯S interstack con-

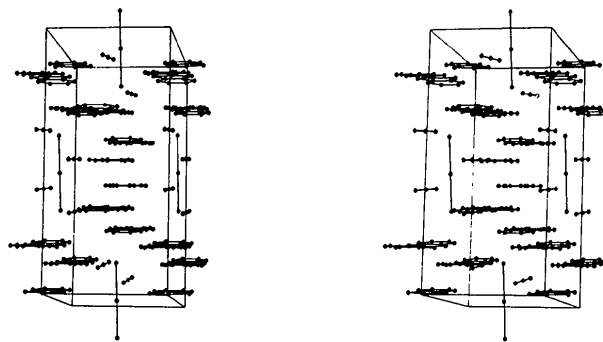


Fig. 1. Packing diagram of compound (1). H atoms have been omitted for clarity.

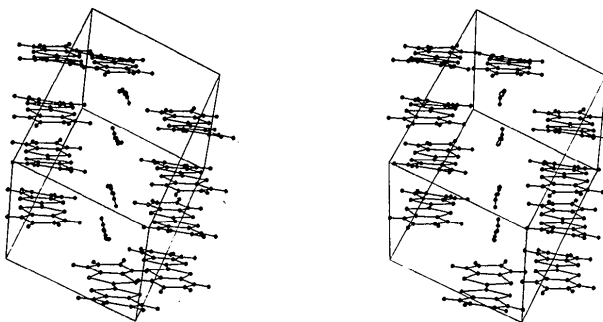


Fig. 2. Packing diagram for compound (2).

tacts. The $Cu(NCS)_2^-$ moiety deviates from linearity, e.g. $N'-Cu-N = 173(1)$ and $Cu-N-C = 166(3)^\circ$, with a $3.055(9)$ Å separation between S' of one molecule and $Cu(-x, -1-y, 1-z)$ of another. In the BEDT-TTF superconducting salts the $Cu(NCS)_2^-$ ions form tricoordinated two-dimensional sheets which lie at the ends of the BEDT-TTF stacks and allow short $S \cdots S$ interstack contacts. The DBTTF ion is slightly bowed with the two planar phenyl rings (0.03 and 0.04 Å r.m.s. deviation) making an angle of $5(1)^\circ$. The EPR spectrum of a single crystal gave a single intense line (width 3.5×10^{-3} T). Attempts to measure the conductivity of the single crystal used for X-ray diffraction studies were unsuccessful, and compressed powders did not maintain their integrity.

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Structure of Dibenzoatodioxouranium(VI)

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Abstract. $[U(C_7H_5O_2)_2O_2]$, $M_r = 512.26$, monoclinic, $C2/m$, $a = 7.604(2)$, $b = 17.408(3)$, $c = 5.296(2)$ Å, $\beta = 95.81(2)^\circ$, $V = 697(2)$ Å³, $Z = 2$, $D_x = 2.44$ Mg m⁻³, $\lambda(Mo K\alpha) = 0.71069$ Å, $\mu = 11.0$ mm⁻¹, $F(000) = 468$, room temperature, $R = 0.058$ for 946 observations with $I > 3\sigma(I)$. The uranyl ion has a fourfold coordination. The coordination polyhedron around the uranium center approximates to an octahedron with the carboxylate groups acting as bridging donors.

Introduction. In the frame of a general study of the complexation of actinides by polycarboxylic ligands, we have undertaken the study of the complexation of

U^{VI} , Np^{VI} and Np^V by benzoic, 2-pyridinecarboxylic and 2,6-pyridinedicarboxylic acids. The aim of this work is to determine the influence of the N atom, which is present in the 2-pyridinecarboxylate and the 2,6-pyridinedicarboxylate, on the complexation, i.e. the nature of the metal–nitrogen bond. In this paper we present the structural study of a uranyl benzoate, benzoic acid being representative of aromatic polycarboxylic acids.

Experimental. Yellow single crystal of dimensions $0.060 \times 0.036 \times 0.330$ mm, grown during the reaction of uranyl hydroxide and benzoic acid in a sealed Pyrex tube at 400 K. Enraf–Nonius CAD-4 diffrac-