

1. Jollès, P. *Angew. Chem.* **76** (1964) 20.
2. Jollès, P. *Proc. Roy. Soc. London. Ser. B* **167** (1967) 350.
3. Chipman, D. M. and Sharon, N. *Science* **165** (1969) 454.
4. Arnon, R. and Schechter, B. *Immunochemistry* **3** (1966) 451.
5. Sanders, M. M., Walsh, K. A. and Arnon, R. *Biochemistry* **9** (1970) 2356.
6. Arnon, R. and Shapira, E. *Biochemistry* **7** (1968) 4196.
7. Fujio, H., Imanishi, M., Nishioka, K. and Amano, T. *Biken J.* **11** (1968) 207.
8. Arnon, R. and Sela, M. *Proc. Natl. Acad. Sci. (U.S.)* **62** (1969) 163.
9. Imanishi, M., Miyagawa, N., Fujio, H. and Amano, T. *Biken. J.* **12** (1969) 85.
10. Bonavida, B. *Federation Proc.* **28** (1969) 326.
11. Atassi, M. Z. and Habeeb, A. F. S. A. *Biochemistry* **8** (1969) 1385.
12. Habeeb, A. F. S. A. and Atassi, M. Z. *Immunochemistry* **6** (1969) 555.
13. Young, J. D. and Leung, C. Y. *Biochemistry* **9** (1970) 2755.
14. Strosberg, A. D. and Kanarek, L. *Eur. J. Biochem.* **14** (1970) 161.
15. Faure, A. and Jollès, P. *FEBS Lett.* **10** (1970) 237.
16. Maron, E., Arnon, R., Sela, M., Perin, J. P. and Jollès, P. *Biochim. Biophys. Acta* **214** (1970) 222.
17. Prager, E. M. and Wilson, A. C. *J. Biol. Chem.* **246** (1971) 5978.
18. Prager, E. M. and Wilson, A. C. *J. Biol. Chem.* **246** (1971) 7010.
19. Arnheim, N., Sobel, J. and Canfield, R. *J. Mol. Biol.* **61** (1971) 237.
20. Canfield, R. E., Kammerman, S., Sobel, J. H. and Morgan, F. J. *Nature New Biol.* **232** (1971) 16.
21. Maron, E., Eshdat, Y. and Sharon, N. *Biochim. Biophys. Acta* **278** (1972) 243.
22. Levy, H. B. and Sober, H. A. *Proc. Soc. Exp. Biol. Med.* **103** (1960) 250.
23. Porath, J., Axén, R. and Ernback, S. *Nature* **215** (1967) 1491.
24. de Saussure, V. A. and Dandliker, W. B. *Immunochemistry* **6** (1969) 77.
25. Helgeland, S. M. and Grov, A. *Acta Pathol. Microbiol. Scand.* **B 79** (1971) 819.
26. Ghuysen, J.-M., Tipper, D. J. and Strominger, J. L. *Methods Enzymol.* **8** (1966) 685.
27. Tipper, D. J. and Strominger, J. L. *Biochem. Biophys. Res. Commun.* **22** (1966) 48.
28. Weber, K. and Osborn, M. *J. Biol. Chem.* **244** (1969) 4406.
29. Grov, A., Oeding, P., Myklestad, B. and Aasen, J. *Acta Pathol. Microbiol. Scand.* **B 78** (1970) 106.

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## On the Structure of $\beta$ -Dy(NH<sub>4</sub>)<sub>3</sub>(SO<sub>3</sub>)<sub>3</sub>·H<sub>2</sub>O

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Several ammonium lanthanoid sulphites can be prepared in the system NH<sub>4</sub><sup>+</sup>—Ln<sup>3+</sup>—SO<sub>2</sub>—H<sub>2</sub>O where Ln=Sm, Gd, or Dy.<sup>1</sup> Because of the low solubility of these phases the crystals are usually very small and cannot be studied by single crystal X-ray methods. After many unsuccessful attempts, however, crystals with suitable dimensions (approximately 0.02 × 0.02 × 0.15 mm<sup>3</sup>) were obtained of the high temperature polymorph of Dy(NH<sub>4</sub>)<sub>3</sub>(SO<sub>3</sub>)<sub>3</sub>·H<sub>2</sub>O by precipitating the compound at 75°C and then gradually warming to 90–95°C. The crystals were kept in a tightly sealed vessel for a week in this temperature range.

Weissenberg and rotation photographs indicated that the needle-shaped crystals have monoclinic symmetry, with the following unit cell dimensions:  $a = 8.88 \text{ \AA}$ ,  $b = 3.98 \text{ \AA}$ ,  $c = 9.48 \text{ \AA}$  and  $\beta = 117.4^\circ$ . The powder pattern was satisfactorily indexed with these unit cell parameters. The measured density, 2.60 g cm<sup>-3</sup>, corresponds to one formula unit in the cell (calculated density 2.65 g cm<sup>-3</sup>). Single crystal intensity data were collected on a Philips PW 1100 computer-controlled four-circle diffractometer, using graphite monochromatized CuK radiation. 439 independent reflections were obtained, representing all observed ( $\sigma(I_{\text{net}})/I_{\text{net}} < 0.25$ ) reflections with  $\theta < 55^\circ$ . There were no systematically absent reflections. The net intensities were corrected for Lorentz and polarization effects as well as for absorption ( $\mu = 338 \text{ cm}^{-1}$ ).

The structure determination was started by assuming the centrosymmetric space group  $P2/m$  (No. 10). A three-dimensional Patterson synthesis revealed presence of the dysprosium atom at the special position  $1(g)$  ( $\frac{1}{2}, 0, \frac{1}{2}$ ), and the subsequent Fourier synthesis gave the positions of the

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Table 1. Fractional atomic coordinates and temperature factors. Estimated standard deviations are given within parentheses.

Atom	Position	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
Dy	1( <i>g</i> )	0.5	0.0	0.5	2.2(1)
S(1)	2( <i>n</i> ) <sup>a</sup>	0.1702(25)	0.5	0.2657(24)	4.0(4)
S(2)	2( <i>n</i> ) <sup>a</sup>	0.4037(25)	0.5	0.7334(24)	4.1(4)
N(1)	2( <i>m</i> )	0.7623(61)	0.0	0.0245(58)	4.7(1.0)
N(2)	1( <i>c</i> )	0.0	0.0	0.5	4.2(1.3)

<sup>a</sup> Occupation number is 0.75.

sulphur and nitrogen atoms. The sulphur atoms were placed at a 2(*n*) position:  $\pm(x, \frac{1}{2}, z)$  with an occupancy of 0.75, and the nitrogen atoms N(1) and N(2) at position 2(*m*):  $\pm(x, 0, z)$  and 1(*c*):  $(0, 0, \frac{1}{2})$ , respectively. A least-squares refinement with isotropic temperature factors resulted in an *R*-value of 12.7%. The atomic parameters are presented in Table 1.

It was not possible, however, to locate the oxygen atoms from the difference Fourier maps, which did not show distinct maxima at expected distances from the sulphur atoms. A careful examination of long exposure Weissenberg and rotation films of several crystals revealed weak superstructure reflections indicating a fourfold *b*-axis. A least-squares refinement of powder data obtained at 25°C with  $\text{CuK}\alpha_1$  radiation ( $\lambda = 1.54050 \text{ \AA}$ ) in a Guinier-Hägg camera, using KCl as an internal standard, gave the following unit cell dimensions for the superstructure (cf. Table 2):  $a = 8.863(6)$ ,  $b = 15.919(5)$ ,  $c = 9.467(5) \text{ \AA}$  and  $\beta = 117.38(5)^\circ$ . The powder pattern was measured and interpreted up to  $\sin^2 \theta = 0.44$ .

The complete structure determination of  $\beta\text{-Dy}(\text{NH}_4)_3(\text{SO}_3)_3 \cdot \text{H}_2\text{O}$  will have to be postponed until intensity data on the superstructure reflections have been measured. However, on the basis of the substructure it can be stated that the atoms are situated in layers  $b/4$  apart and that the sulphite groups are coordinated to dysprosium through oxygen. The Dy-S distances of 3.40 Å and 3.41 Å exclude other possibilities. The IR absorption spectrum gives further support for the bonding through oxygen. In the region 2000–400  $\text{cm}^{-1}$  there are, besides maxima due to water (1665w) and ammonium (1395s), four bands (1020m, 960s, 890vs, 820s) in the S-O stretching region

Table 2. X-Ray powder data of  $\beta\text{-Dy}(\text{NH}_4)_3(\text{SO}_3)_3 \cdot \text{H}_2\text{O}$ .  $\text{CuK}\alpha_1$  radiation ( $\lambda = 1.54050 \text{ \AA}$ ).

<i>h</i>	<i>k</i>	<i>l</i>	$10^5 \sin^2 \theta_{\text{obs}}$	$10^5 \sin^2 \theta_{\text{obs}}$	<i>I</i> <sub>obs</sub>
0	0	1	837	839	s
1	0	0	963	958	s
1	2	0	1890	1894	vw
1	0	1	2624	2622	m
2	0	0	3837	3831	w
0	4	1	4576	4585	w
1	4	0	4702	4704	m
1	4	1	6364	6368	s
-2	4	1	6736	6767	m
0	4	2	7074	7104	m
0	0	3	7561	{ 7555	w
2	4	0		{ 7577	
3	0	0	8599	8620	w
-3	2	3	9698	{ 9690	w
1	4	2		{ 9711	
2	4	1	10070	10066	w
2	0	2	10501	10488	w
-2	0	4	10670	10665	w
1	0	3	10964	10987	vw
1	6	1	11045	11051	vw
1	1	3	11253	11222	vw
-2	6	2	12338	{ 12319	w
-4	1	2		{ 12319	
3	4	0		{ 12366	
2	4	2	14240	14234	w
1	4	3	14709	14733	w
-4	3	1	14966	14973	m
3	4	1	15683	15680	w
-4	1	4	15792	15795	w
2	5	2	16341	16241	vw
-2	5	4	16531	16518	w
-1	5	4	16949	16944	vw
1	8	1	17599	17606	w
-1	2	5	18781	{ 18758	w
2	8	0		{ 18815	
0	7	3	19010	{ 19027	w
3	3	2		{ 19034	

( $\nu_1$  and  $\nu_3$  vibrations). The maximum at  $630\text{ cm}^{-1}$  can be attributed to the  $\nu_2$  vibration, and the last two modes ( $525\text{m}$ ,  $460\text{m}$ ) are probably due to the  $\nu_4$  vibration. The nondegeneracy of the  $\nu_3$  and  $\nu_4$  vibrations as well as the existence of a high intensity maximum at  $960\text{ cm}^{-1}$  are in agreement with oxygen coordination,<sup>2,3</sup> although the occurrence of a band at  $1020\text{ cm}^{-1}$  (if not an overtone or a combination band) complicates the interpretation.

The ammonium ions are situated at the edges of the unit cell and are possibly connecting the structure in the directions of the *a* and *c* axes *via* hydrogen bonding.

As the superstructure reflections are very weak they may be due to the oxygen atoms only. On the other hand, the temperature factors for the sulphur and nitrogen atoms are high, although not unreasonable (*cf.* Table 1).

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1. Erämetsä, O., Niinistö, L. and Korvela, T. *Suomen Kemistilehti* **B 45** (1972) 394.
2. Newman, G. and Powell, D. B. *Spectrochim. Acta* **19** (1963) 213.
3. Nyberg, B. and Larsson, L. *Acta Chem. Scand.* **27** (1973) 63.

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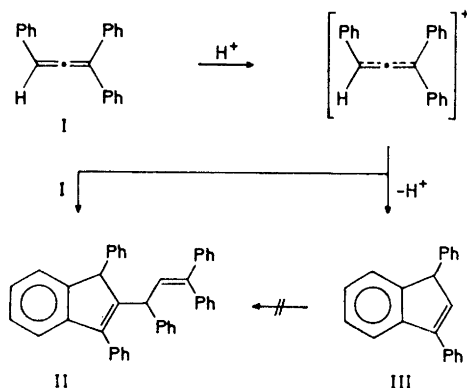
## The Acid-catalyzed Reactions of Triphenylallene. A Reexamination

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Acid-catalyzed rearrangement of triphenylallene (I) has been reported to give a dimeric product,  $\text{C}_{42}\text{H}_{32}$ .<sup>1</sup> To this product, which also was formed by acid-catalyzed dehydration of 1,3,3-triphenylprop-2-en-1-ol and 1,1,3-triphenylprop-2-en-1-ol,<sup>2,3</sup> Jones<sup>4</sup> and Rewicki<sup>5</sup> independently assigned structure II. In analogy with the formation of 1,3,3-triphenylindene from tetraphenylallene,<sup>6</sup> 1,3-diphenylindene (III) was the expected product; this was isolated in 40% yield from the reaction of the above mentioned allylic alcohols with phosphorus pentoxide.<sup>2</sup> We want to report that compound III is also formed by treatment of triphenylallene with acid.

The reaction of I with HCl/acetic acid gave besides the dimer a small amount of another component which was isolated. The NMR spectrum showed a vinyl proton at  $\delta$  6.6 coupled to a methine proton at  $\delta$  4.6 ( $J = 2\text{ Hz}$ ) and aromatic protons at  $\delta$  7.0–7.7. The mass spectrum ( $m/e$  268) corresponded to the indene III. The isomeric 3,3-diphenylindene was not present.



The formation of the dimer has been suggested to proceed through the addition of an allylic carbonium ion to another

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