Structure of the Triselenourea Ion in the Dichloride and Dibromide Salts

SVERRE HAUGE, DAVID OPEDAL and JON AARSKOG

Chemical Institute, University of Bergen, Bergen, Norway

As part of a study of linear three-selenium systems,[1] crystal structure analyses of triselenourea dichloride hydrate, $[SeC(NH_2)_2]_3Cl_2 \cdot H_2O$ (I), and triselenourea dibromide hydrate, $[SeC(NH_2)_2]_3Br_2 \cdot H_2O$ (II), are carried out. These compounds were first prepared and described by Verneuil.[2]

The dichloride was prepared by oxidation of a cold hydrochloric acid solution of selenourea with sodium hypochlorite. One recrystallization from 2 N hydrochloric acid gave reddish brown prisms. The dibromide was prepared as described by Verneuil,[2] through air oxidation of a hydrobromic acid solution of selenourea.

The formation reaction:

$$3 SeC(NH_2)_2 = [SeC(NH_2)_2]_3^{2+} + 2e$$

is analogous to those of the trihalide ions, and the triselenocyanate ion:[1-3]

$$3 SeCN^- = (SeCN)_3^- + 2e$$
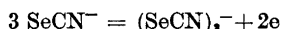
The crystals of the two compounds are isomorphous, with $a = 12.202(5)$ Å, $b = 18.142(7)$ Å, and $c = 12.232(5)$ Å for I, and $a = 12.604(5)$ Å, $b = 18.268(7)$ Å, and $c = 12.512(5)$ Å for II. The space group is *Pbca* (No. 61), and there are eight formula units per unit cell; density, calc. 2.25, found 2.26 g/cm³ for I, and calc. 2.52, found 2.55 g/cm³ for II. The intensities were estimated visually from integrated Weissenberg photographs around the *a* and *c* axes, taken with CuKα radiation using the multi-film technique. For each compound, about 1700 reflections were observed with measurable intensities, from the ten layers $0kl - 7kl$ and $hk0 - hk1$. The intensities were at later stages corrected for absorption and for secondary extinction.

The structures were solved by three-dimensional Patterson and Fourier methods using the heavy-atom technique. Full-matrix least squares refinements with anisotropic temperature factors brought the reliability index, *R*, down to 0.056 for

I and 0.063 for II. The coordinates of the heavy atoms at the present stage are listed in Table 1.

Table 1. Atomic coordinates.

	x	y	z
I			
Se_1	0.2809	0.2713	0.1656
Se_2	0.2524	0.4128	0.1794
Se_3	0.2447	0.5625	0.1846
Cl_1	0.0606	0.1042	0.4730
Cl_2	0.0565	0.3963	0.4649
II			
Se_1	0.2786	0.2740	0.1653
Se_2	0.2524	0.4161	0.1796
Se_3	0.2460	0.5644	0.1848
Br_1	0.0617	0.1018	0.4744
Br_2	0.0585	0.3956	0.4699

The triselenourea ion in I is shown in Fig. 1. In both compounds the $Se_1 - Se_2 - Se_3$ angle is 174° and the $C_2 - Se_2 - Se_1$ and $C_2 - Se_2 - Se_3$ angles are 89°. The $Se_1 - Se_2$ bond lengths are 2.60 Å in I and 2.62 Å in II, and the $Se_2 - Se_3$ bond lengths are 2.72 Å in I and 2.71 Å in II. These values for Se—Se bond lengths,
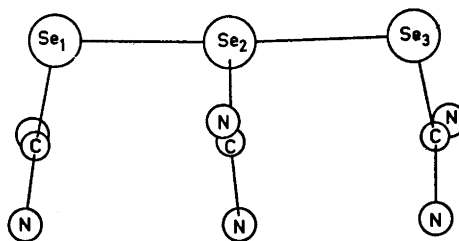

Fig. 1. The triselenourea ion in $[SeC(NH_2)_2]_3Cl_2 \cdot H_2O$, as seen normal to a plane through Se_1 and Se_3 passing approximately equidistant from C_2 and from C_1 and C_3.

particularly the total lengths of the very nearly linear three-selenium systems, are close to the values found in the triselenocyanate ion.[1,3]

The selenourea groups of an ion are planar and approximately parallel, the plane of the middle (Se_2) selenourea group making angles of 15° and 5°, respectively, with the planes of the terminal (Se_1 and Se_3) selenourea groups, in both compounds. The three selenium atoms and the carbon atoms of the terminal selenourea groups lie approximately in the same plane; this plane makes an angle of about 75° with the plane of the three selenium atoms and the carbon atom of the middle selenourea group.

There is a close non-bonded contact between the middle selenium atom Se_2 and a halide ion X^-, 3.46 Å in I and 3.53 Å in II, at a $C-Se\cdots X$ angle of 175°. A close non-bonded contact also occurs between Se_3 and a halide ion, 3.70 Å in I and 3.72 Å in II, at a $C-Se\cdots X$ angle of 165.°

A full account of the work will be published later.

1. Foss, O. In Andersen, P., Bastiansen, O. and Furberg, S. *Selected Topics in Structure Chemistry*, Universitetsforlaget, Oslo 1967, p. 145.
2. Verneuil, A. *Ann. Chim. Phys.* [6] **9** (1886) 289.
3. Foss, O. and Hauge, S. *Acta Chem. Scand.* **17** (1963) 1807.

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## Studies on Orchidaceae Alkaloids

XIX.* Synthesis and Absolute Configuration of Dendrine

INGRID GRANELLI and KURT LEANDER

Department of Organic Chemistry, University of Stockholm, Sandåsgatan 2, S-113 27 Stockholm, Sweden

Dendrine,[1] a minor alkaloid from *Dendrobium nobile* Lindl., has been assigned the structure I, with only the configuration at C-14 undetermined. In the present communication a synthesis of dendrine (I) by a Reformatsky reaction on dendrobine immonium bromide (III) is reported.

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* For No. XVIII of this series, see Ref. 1.

II Dendrobine

III

I Dendrine

IV Dendrine C-14 epimer
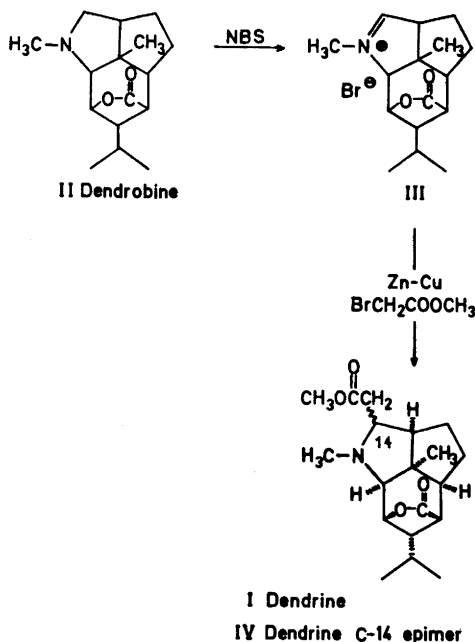
Oxidation of dendrobine (II) with *N*-bromosuccinimide in ether-acetone afforded the immonium salt III.[2] By reacting III with methylbromoacetate and zinc-copper couple in *N*,*N*-dimethylformamide at 100°, two bases were formed. The major product, m.p. 188−189°, $[\alpha]_D^{26}$ −80° (c 0.17, chloroform), has properties (NMR, IR, MS, GLC, TLC) indistinguishable from those of authentic dendrine (I), except for specific optical rotation which was previously reported to be $[\alpha]_D^{13}$ −114° (c 0.85, chloroform).[3] However, our measurement of optical rotation of authentic dendrine (I), $[\alpha]_D^{24}$ −81° (c 0.14, chloroform), was very close to the specific rotation of the synthetic product reported herein.

The minor product (IV) was obtained as a gum, $[\alpha]_D^{20}$ +23° (c 0.57, chloroform). Its mass spectrum was indistinguishable, except for small differences in intensities of some of the peaks, from that given by dendrine (I). The similarity of the mass spectra of I and IV suggests that the bases are epimers, which is further supported by their IR and NMR spectra.

In the synthesis, the epimers I and IV were formed in the ratio 15:1. The Reformatsky reagent preferably attacks the