

Correlation between the Structure and Reactivity of the Selenide Dihalide of the New Reducing Reagent $\text{NaBH}_4\text{-R}_2\text{SeX}_2$ on the Highly Selective Reduction of Amides. X-Ray Molecular Structure of Bis-(2-chloroethyl)selenium Dichloride

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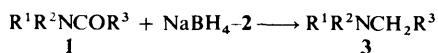
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Treatment of NaBH_4 with a diethylselenium dihalide generates borane which reduces amides to the corresponding amines. The reduction abilities of the reductants depend on the structure [that is, trigonal-bipyramidal (TB) or molecular complex (MC)] of **2**. The order of the reduction ability is as follows: $\text{NaBH}_4\text{-diiodide } \mathbf{2c} > \text{NaBH}_4\text{-dibromide } \mathbf{2b} > \text{dichloride } \mathbf{2a}$. The reagents, $\text{NaBH}_4\text{-2b}$ and $\text{NaBH}_4\text{-2a}$, which form TB structures can reduce the tertiary amide with high selectivity, while $\text{NaBH}_4\text{-2c}$, which forms a molecular complex, reduces primary, secondary and tertiary amides non-selectively.

It is well known¹ that amides can be reduced to amines with lithium aluminium hydride, diborane, or by catalytic hydrogenation, although high temperatures are required for the last method. Even with LiAlH_4 the reaction is more difficult than the reduction of most other functional groups, and often other groups may be reduced without disturbing the amide function. However, the reduction of primary, secondary, and tertiary amides[†] under ordinary conditions, *i.e.* with an excess of the reducing agent present, usually produces the corresponding amines,²⁻⁴ although in some cases reductive cleavage takes place. Although amides are not generally reduced with sodium borohydride itself,⁵ they are reduced with a combination of $\text{NaBH}_4\text{-pyridine}$,^{5,6} $\text{NaBH}_4\text{-TiCl}_4$,⁷ $\text{NaBH}_4\text{-CoCl}_2$,⁸ or $\text{NaBH}_4\text{-SnCl}_4$.⁹ Furthermore, the Vilsmeier complexes of tertiary and secondary amides can be reduced with NaBH_4 in high yield.^{10,11} Diborane is also a good reducing agent for all three types of amides,¹² although in some cases cleavage takes place and the aldehyde or alcohol is obtained. As already described, many reagents can reduce tertiary, secondary and primary amides non-selectively. In previous papers^{13,14} we reported the highly selective reduction of tertiary amides (among tertiary, secondary and primary amides) to the corresponding tertiary amines using $\text{NaBH}_4\text{-dialkylselenium dibromides}$. Now, it is known^{15,16} that the structure of the 1:1 adduct of dimethyl selenide with a halogen depends on the type of halogen atom; that is, chlorine and bromine adducts form a trigonal-bipyramidal structure (TB), whereas the structure of the adduct with iodine is a molecular complex (MC) as shown in Fig. 1. We report here the correlation between the structures of the 1:1 adducts (**2**) of diethyl selenide with halogens and the reduction abilities of the complexes $\text{NaBH}_4\text{-2}$ in the reduction of formamides to the corresponding amines.

The reaction was carried out in stirred mixtures of an amide **1** (5 mmol), NaBH_4 (25 mmol) and reagent **2** (5 mmol) in



1a, 3a	$\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{H}$	Et_2SeX_2
1b, 3b	$\text{R}^1 = \text{Ph}, \text{R}^2 = \text{R}^3 = \text{H}$	2a ; X = Cl
1c, 3c	$\text{R}^1 = \text{Ph}, \text{R}^2 = \text{Me}, \text{R}^3 = \text{H}$	2b ; X = Br
1d, 3d	$\text{R}^1 = \text{R}^2 = \text{H}, \text{R}^3 = \text{Ph}$	2c ; X = I
1e, 3e	$\text{R}^1 = \text{Me}, \text{R}^2 = \text{H}, \text{R}^3 = \text{Ph}$	
1f, 3f	$\text{R}^1 = \text{R}^2 = \text{Me}, \text{R}^3 = \text{Ph}$	

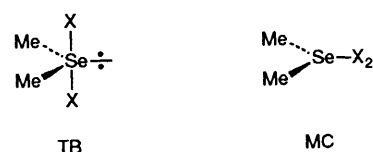
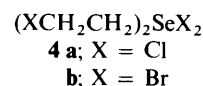


Fig. 1 Structure of the 1:1 adduct of dimethyl selenide with halogen

tetrahydrofuran (THF) (50 cm^3) at 65 °C. After the usual work-up, the products were analysed by HPLC (Table 1).

In general, the reduction abilities of the complexes $\text{NaBH}_4\text{-2}$ to form the corresponding amines from the amides followed the order $\text{NaBH}_4\text{-2c} > \text{NaBH}_4\text{-2b} > \text{NaBH}_4\text{-2a}$. For example, $\text{NaBH}_4\text{-2c}$ can reduce the tertiary, secondary and primary amides non-selectively. Also, the reduction of tertiary, secondary and primary amides with reagent $\text{NaBH}_4\text{-I}_2$ proceeded in high yield non-selectively. However, $\text{NaBH}_4\text{-2b}$ cannot reduce the primary and secondary amides, although $\text{NaBH}_4\text{-2a}$ can reduce the secondary amide, albeit in very low yield (12%). Similar results were obtained when using $\text{NaBH}_4\text{-bis-(2-chloroethyl)selenium dichloride } \mathbf{4a}$ and $\text{NaBH}_4\text{-bis-(2-bromoethyl)selenium dibromide } \mathbf{4b}$ as reducing agents.



The conversion course of the reduction of *N*-methylformamide **1c** when using species $\text{NaBH}_4\text{-2}$ as a reducing agent in THF at 65 °C is shown in Fig. 2. When the diiodide **2c** was used as the reducing agent, the reduction rate was remarkably high, but this was considerably reduced with the other reagents **2a** and **2b**. The order of reduction rate is given by **2c** > **2b** > **2a**. One possible reason for the greater selectivity of the bromine adduct **2b** over the chlorine adduct **2a** is attributed to the similarity in size between Se and Br, although differences in the reduction ability between species **2b** and **2a** cannot be detailed at present. The results suggest that molecular iodine is formed more rapidly by dissociation of species **2c** compared with the

[†] In this paper the terms secondary and tertiary amides are used non-systematically to refer to *N*-substituted and *N,N*-disubstituted primary amides RCONHR' and $\text{RCONR}'\text{R}''$.

Table 1 Reduction of amides to amines with $\text{NaBH}_4\text{-Et}_2\text{SeX}_2$ **2**^a

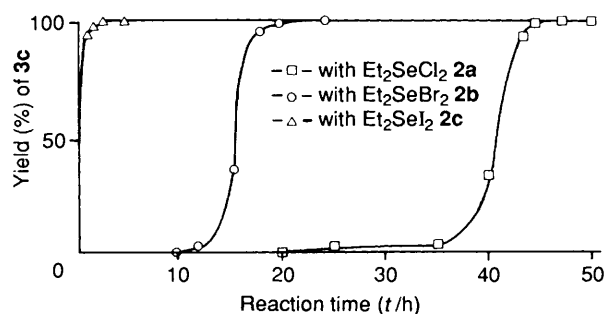
Comp.	Reducing agent 2 ^b	Reaction time (t/h)	Product ^c and yield (%) ^d	M.p. or B.p. (°C) (lit./°C)
1a	2a	20	3a 0 ^e	224–226 (227–228) ^{f,17}
	2b	20	3a 0 ^e	
	2c	20	3a 50 ^e	
1b	2a	20	3b 12	87–90/14 mmHg ^g (194–196) ^{f,18}
	2b	20	3b 0	
	2c	1	3b 100	
1c	2a	50	3c 100	80–83/14 mmHg ^g (192–194) ^{f,19}
	2b	20	3c 100	
	2c	0.5	3c 99	
1d	2a	50	3d 0	246–248 (253) ^{f,20}
	2b	24	3d 0	
	2c	24	3d 41	
1e	2a	50	3e 0	175–178 (178) ^{f,21}
	2b	50	3e 0	
	2c	50	3e 10	
1f	2a	20	3f 4	174–176 (175) ^{f,21}
	2b	20	3f 3	
	2c	20	3f 64	

^a THF (50 cm³) was used as solvent and the reaction was carried out at refluxing temperature. ^b Amides (1.0 mol equiv.), NaBH_4 (5.0 mol equiv.) and reagent **2** (1.0 mol equiv.) were used. ^c Products were identified by (i) comparison of spectral data (IR, ¹H NMR, mass) with literature data, and (ii) in most cases, by the addition of authentic material upon HPLC analysis. ^d Determined from the calibration course of the authentic sample by HPLC. ^e Isolated yield as HCl salt. ^f M.p. ^g B.p.

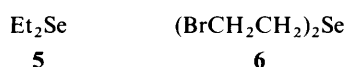
Table 2 Reduction of amides **1b** and **1c** to amines with $\text{NaBH}_4\text{-X}_2$ **a**

Comp.	X ^b	Reaction time (t/h)	Product and yield (%) ^c
1b	Br	3	3b 27
	Br	20	3b 92
	I	0.5	3b 94
	I	1	3b 100
1c	Br	1	3c 0
	Br	20	3c 100
	I	0.5	3c 72
	I	6	3c 99

^a THF (50 cm³) was used as solvent and the reaction was carried out at reflux temperature. ^b Amides (1.0 mol equiv.), NaBH_4 (5.0 mol equiv.) and Br_2 (1.0 mol equiv.) were used. ^c Determined from the calibration course of the authentic sample by HPLC.

**Fig. 2** The conversion course of *N*-methylformanilide **1c** using the complex $\text{NaBH}_4\text{-2}$

formation of a bromine or chlorine molecule from **2b** and **2a**, due to the weaker bond energy of a Se–I bond than that of Se–Br and Se–Cl bonds.²² Reaction of the resulting iodine with sodium borohydride gives borane. Therefore, reduction of the amides by using $\text{NaBH}_4\text{-2c}$ or $\text{NaBH}_4\text{-I}_2$ showed very similar results. However, the dissociation of the dibromide and dichloride **2b** and **2a** to diethyl selenide **5** and a halide is slower than that of the diiodide **2c**. Therefore, the reductive power of species $\text{NaBH}_4\text{-2b}$ and $\text{NaBH}_4\text{-2a}$ is relatively weak compared



with that of complex $\text{NaBH}_4\text{-2c}$ and showed some selectivity. This assumption can be supported from the dissociation constants (2.12×10^{-3} and 4×10^{-7} , respectively) of dimethylselenium diiodide and dimethylselenium dibromide in carbon tetrachloride.²³ It is also noteworthy that formamide derivatives **1b** and **1c**, but not formamide **1a** itself, were more easily reduced with the reducing agents than were the benzamide derivatives **1d–f**. The more difficult reduction of benzamide derivatives may be attributed to the steric and resonance effects due to the phenyl group attached to the carbonyl carbon atom. In order to investigate the role of species Et_2SeX_2 **2**, reductions of the secondary and tertiary amides **1b** and **1c** with $\text{NaBH}_4\text{-X}_2$ were carried out and the results are summarized in Table 2. The reaction of compounds **1b** and **1c** with $\text{NaBH}_4\text{-I}_2$ proceeded more rapidly than did that with $\text{NaBH}_4\text{-Br}_2$ as reducing reagent. In this reaction, the $\text{NaBH}_4\text{-Br}_2$ reagent can reduce secondary and tertiary amides non-selectively, while the $\text{NaBH}_4\text{-2b}$ reagent will only reduce tertiary amides with high selectivity. However, the $\text{NaBH}_4\text{-I}_2$ reagent showed a similar reduction ability to that of $\text{NaBH}_4\text{-2c}$. These results suggest that the reaction of a bromine molecule with NaBH_4 gave borane and that the resulting borane acts as a reducing reagent. Our selective reduction of tertiary amides to the corresponding amines may be due to the difference in the reducing ability of the 1:1 complex of 5-BH_3 ^{13,14} and THF-BH_3 ,^{12,24} which can reduce the amides non-selectively, because the combination of NaBH_4 with reagents **2a** and **2b** can selectively reduce tertiary amides as described in previous papers.^{13,14} However, one cannot rule out the possibility that the 1:1 borane complex with the dihalide **2b** or **2a** acts as the selective reducing reagent, because it was reported that the reaction of dialkylselenium dibromides with boron tribromide gave a 1:1 complex.²⁵ However, this possibility was ruled out since the reaction of dibromide **2b** with borane gave diethyl selenide **5** instead of the 2b-BH_3 complex.

To examine the correlation between the structure of the selenides **2** and the reduction ability of reagents $\text{NaBH}_4\text{-2}$, the ¹H and ¹³C NMR chemical shifts of compounds **2c**, **2b**, **2a**, **4b**, **5** and bis-(2-bromoethyl) selenide **6** have been measured (Table 3). The differences in the ¹H chemical shifts due to the methylene protons and the methyl protons of compounds **2b** and **2a** from those of diethyl selenide **5** are ~1.28 and 1.31, 0.33 and 0.35 ppm, respectively, although the chemical-shift values of the methylene and the methyl protons in the iodine adduct **2c** are

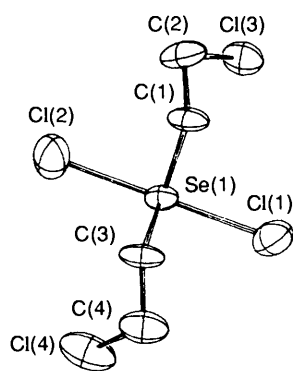
Table 3 ^1H and ^{13}C chemical shifts (δ) of compounds **2a**, **2b**, **2c**, **4b**, **5** and **6**^{a-c}

Comp.	^1H		^{13}C	
	CH ₂	Me (or BrCH ₂)	CH ₂	Me (or BrCH ₂)
Et ₂ Se 5	2.54	1.36	16.68	16.17
Et ₂ SeCl ₂ 2a	3.85 (1.31)	1.71 (0.35)	57.10 (40.42)	10.16 (-6.01)
Et ₂ SeBr ₂ 2b	3.82 (1.28)	1.69 (0.33)	55.20 (38.52)	10.58 (-5.59)
Et ₂ SeI ₂ 2c	2.88 (0.34)	1.44 (0.08)	26.08 (9.40)	14.44 (-1.73)
(BrCH ₂ CH ₂) ₂ Se 6	3.10	3.68	25.63	30.70
(BrCH ₂ CH ₂) ₂ SeBr ₂ 4b	4.30 (1.20)	4.17 (0.49)	60.30 (34.67)	23.96 (-6.74)

^a The NMR spectra were measured on a JEOL JNM GX-400FT spectrometer. ^b ^1H and ^{13}C NMR spectra were measured in [$^2\text{H}_6$]THF (**2a**, **2b**, **2c** and **5**) or CDCl_3 (**4b** and **6**). ^c A downfield shift is denoted by a positive value. Chemical-shift differences from the data for compound **5** or **6** are presented in parentheses.

Table 4 Fractional atomic co-ordinates ($\times 10^4$), with estimated standard deviations in parentheses

Atom	x	y	z
(a) Compound 4a			
Se	1 782.6(10)	926.9(6)	1 674.6(9)
Cl(1)	564(3)	552(2)	3 537(3)
Cl(2)	3 021(4)	1 267(2)	-169(3)
Cl(3)	4 889(3)	-906(2)	3 393(3)
Cl(4)	-2 084(3)	1 906(2)	-378(3)
C(1)	4 109(9)	1 258(6)	2 899(10)
C(2)	5 522(11)	368(7)	2 794(12)
C(3)	827(9)	2 447(6)	1 624(9)
C(4)	-1 141(12)	2 470(8)	1 209(12)
(b) Compound 4b			
Se	10 006(8)	1 305(2)	10 003(6)
Br(1)	6 713(5)	1 213(3)	8 682(3)
Br(2)	13 203(5)	1 189(3)	11 309(3)
Br(3)	12 843(6)	4 148(4)	8 363(3)
Br(4)	7 146(6)	4 218(4)	11 594(3)
C(1)	10 980(39)	2 439(27)	8 936(22)
C(2)	12 151(78)	3 455(39)	9 641(45)
C(3)	9 121(45)	2 920(43)	10 636(37)
C(4)	7 902(56)	2 665(37)	10 974(45)

**Fig. 3** A perspective view of compound **4a** with the atom-numbering scheme

only 0.34 and 0.08 ppm, respectively. Similar results were obtained for the ^{13}C chemical shifts of compounds **2a**, **2b** and **2c**. The methylene carbon peaks of compounds **2b** and **2a** are shifted downfield by ~ 38.52 and 40.42 ppm, respectively, compared with that of compound **5**. However, the methylene carbon peaks of the diiodide **2c** are shifted downfield by only ~ 9.40 ppm from that of the selenide **5**. Similar chemical-shift

Table 5 Bond lengths (\AA) and angles ($^\circ$), with estimated standard deviations in parentheses, for compound **4a**

Bond lengths			
Se-Cl(1)	2.376(2)	Cl(3)-C(2)	1.783(9)
Se-Cl(2)	2.360(3)	Cl(4)-C(4)	1.751(12)
Se-C(1)	1.953(7)	C(1)-C(2)	1.558(9)
Se-C(3)	1.987(7)	C(3)-C(4)	1.467(8)
Bond angles			
Cl(1)-Se-Cl(2)	178.9(1)	C(1)-Se-C(3)	95.6(1)
Cl(1)-Se-C(1)	90.2(3)	Se-C(1)-C(2)	110.7(4)
Cl(1)-Se-C(3)	89.0(3)	Cl(3)-C(2)-C(1)	109.0(4)
Cl(2)-Se-C(1)	89.5(3)	Se-C(3)-C(4)	112.0(4)
Cl(2)-Se-C(3)	92.1(3)	Cl(4)-C(4)-C(3)	114.7(6)

differences in the ^1H and ^{13}C NMR spectra of compound **4b** from compound **6** were also observed. The magnitude and the direction of the chemical-shift changes of compounds **2b**, **2a** and **4b** from those of compound **5** or **6** suggest that the structures of these adducts (**2a**, **2b** and **4b**) are of the trigonal-bipyramidal form.¹⁶ Slight ^1H and ^{13}C chemical-shift differences of adduct **2c** from the selenide **5** should be due to the formation of the molecular complex.¹⁶

In order to investigate the structures in more detail, an X-ray analysis of compound **4a** and **4b** was carried out, although X-ray analyses of adducts **2c**, **2b** and **2a** could not be carried out because we failed to isolate a single crystal at room temperature despite many attempts. The final atomic parameters for adducts **4a** and **4b** are listed in Table 4 and the molecular structure for the former compound is illustrated in Fig. 3. In addition the bond lengths and angles for **4a** are listed in Table 5. As shown in Fig. 3, the two chlorine atoms attached to the selenium atom are situated in a *trans* configuration and the Cl(1)-Se-Cl(2) angle is $178.9(1)^\circ$, which deviates slightly from the expected 180° . Also, the bond angle C(1)-Se-C(3) is $95.6(1)^\circ$. The Cl-Se bond lengths of 2.376(2) and 2.360(3) \AA are in agreement with the reported values for the linear Cl-Se bond.²⁶ In addition, Se-C(1) and Se-C(3) are 1.953(7) and 1.987(7) \AA , respectively. Therefore, the selenium atom forms a slightly distorted trigonal-bipyramidal geometry with two axially co-ordinated chlorine atoms. Furthermore, the structure of the bromine adduct **4b** is very similar with that of compound **4a**, although the *R*-value is still 0.091 in spite of the many refinements that were attempted.*

* Compound **4b**: Bond lengths and angles; Se-Br(1) 2.576(15) \AA , Se-Br(2) 2.536(15) \AA , Se-C(1) 2.21(5) \AA , Se-C(3) 2.07(9) \AA , Br(3)-C(2) 2.23(7) \AA , Br(4)-C(4) 2.022(7) \AA , Br(1)-Se-Br(2) $175.0(6)^\circ$, C(1)-Se-C(3) $90.0(3)^\circ$.

In conclusion, the reduction ability of complexes $\text{NaBH}_4\text{-2}$ as reducing reagents of amides to amines depends on the structure of the halogen adducts **2**, and the reagents $\text{NaBH}_4\text{-2b}$ or -2a , which form trigonal-bipyramidal structures, show low reducing ability toward primary and secondary amides. Therefore, complexes $\text{NaBH}_4\text{-2a}$ and $\text{NaBH}_4\text{-2b}$ can reduce tertiary amides with high selectivity, whereas $\text{NaBH}_4\text{-2c}$ (MC structure) reduces the amides to the corresponding amines non-selectively.

Experimental

M.p.s were recorded with a Yazawa micro m.p. apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were determined in $[\text{D}_6]\text{THF}$ with a JEOL JNM GX-400 FT spectrometer. High performance liquid chromatography (HPLC) was carried out on a JASCO HPLC system with a Finepak SIL, $\text{C}_{18}\text{-5}$ column (4.6×250 mm I.D., $5 \mu\text{m}$ particle size) monitored by UV absorption measurements.

Materials.—Diethylselenium dichloride **2a**,²⁷ diethylselenium dibromide **2b**,²⁷ diethylselenium diiodide **2c**,²⁸ bis-(2-chloroethyl)selenium dichloride **4a**,²⁹ bis-(2-bromoethyl)selenium dibromide **4b**,³⁰ diethyl selenide **5**³¹ and bis-(2-bromoethyl)selenide **6**³² were prepared according to the methods reported in the literature. All compounds purchased from commercial sources were used without further purification, and all solvents were purified by distillation in the usual manner.

General Procedure for the Reduction of Amides with $\text{NaBH}_4\text{-2}$.—A suspension of *N*-methylbenzamide **1e** (0.68 g, 5 mmol), the iodide **2c** (1.95 g, 5 mmol), and sodium borohydride (0.95 g, 25 mmol) in THF (50 cm^3) was stirred for 20 h at reflux. After the reaction mixture was cooled to room temperature, water (30 cm^3) was added. The aq. solution was extracted with diethyl ether and the extract was concentrated. The yield of the product was determined by HPLC with an internal standard. The yield of product **3e** was 50%. The reduction of compound **1a** using the dihalide **2a** or **2b** was similarly carried out (reaction time 20 h). However, the reduction product **3e** could not be obtained and the starting material **1e** was recovered quantitatively.

General Procedure for the Reduction of Amides with $\text{NaBH}_4\text{-X}_2$.—To a THF solution (100 cm^3) containing formamide **1a** (1.32 g, 30 mmol) and iodine (7.41 g, 30 mmol) was quickly added sodium borohydride (5.50 g, 150 mmol). After the mixture had been stirred under reflux for 20 h, it was cooled to room temperature. To the mixture was added water (20 cm^3) and 6 mol dm^{-3} aq. HCl (30 cm^3). The aq. solution was extracted with diethyl ether ($30 \text{ cm}^3 \times 3$) and then the aq. solution was concentrated under reduced pressure. The resulting solid was dissolved in water (50 cm^3) and then sodium hydroxide was added to the solution until it became basic (pH paper). The basic solution was heated and the evaporating gas was absorbed into 6 mol dm^{-3} aq. HCl. The solution was concentrated under reduced pressure and the resulting solid was recrystallized from ethanol to give the HCl salt of compound **3a** in 63% yield.

General Procedure for the Reduction of Compounds **1 with $\text{BH}_3\text{-2}$.**—To a solution of compound **1c** (0.71 g, 5 mmol) and compound **2a** (4.14 g, 5 mmol) in THF (30 cm^3), a THF solution (5 cm^3) of borane (5 mmol) was added. After the mixture had been stirred under reflux for 29 h, the mixture was cooled to room temperature and then the supernatant solution was analysed by HPLC. The yield of compound **3c** was 98%.

Crystallographic Data.—Crystals of dimensions $0.4 \times 0.1 \times$

0.05 , and $0.5 \times 0.2 \times 0.1$ mm for compounds **4a** and **4b** were used for X-ray crystallography. For **4a**: $\text{C}_4\text{H}_8\text{Cl}_4\text{Se}$, $M_r = 276.6$, monoclinic, space group $P2_1/c$, $a = 7.691(1)$, $b = 12.178(2)$, $c = 10.267(3)$ Å, $\beta = 104.55(1)$, $V = 930.8$ Å³, $Z = 4$, $D_c = 1.97$ g cm^{-3} , $\mu(\text{Cu-K}\alpha) = 160$ cm^{-1} . For **4b**: $\text{C}_4\text{H}_8\text{Br}_4\text{Se}$, $M_r = 454.4$, monoclinic, space group Aa , $a = 7.520(2)$, $b = 10.268(2)$, $c = 14.201$ Å, $\beta = 108.74(1)^\circ$, $V = 1038.5$ Å³, $Z = 4$, $D_c = 2.91$ g cm^{-3} , $\mu(\text{Mo-K}\alpha) = 193$ cm^{-1} .

Intensity data were recorded on a Rigaku AFC-5R diffractometer using graphite-monochromatized Cu-K α radiation ($2\theta < 128^\circ$) for **4a**, and graphite-monochromatized Mo-K α radiation ($2\theta < 50^\circ$) for **4b**. Of the 1533 and 917 independent reflections measured, only 1461 and 747 were considered as being observed with $F_o > 2\sigma(F_o)$ for compounds **4a** and **4b**, respectively. All intensities were corrected for Lorentz and polarization effects, and an empirical absorption correction, based on ψ -scan data, was applied. Both structures were solved by the heavy-atom method. Positions of hydrogen atoms were estimated from standard geometry. The final refinements using block-diagonal least-squares methods with anisotropic temperature factors for the non-hydrogen atoms and isotropic temperature factors for the hydrogen atoms lowered the R -values to 0.072 [$R_w = 0.078$, $w = 1/\sigma^2(F_o)$], and 0.091 [$R_w = 0.130$, $w = 1/\sigma^2(F_o)$] for **4a** and **4b**, respectively.

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