Uranyl Complexes of Acetamidoxime and Benzamidoxime. Preparation, Characterization, and Crystal Structure

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The uranyl complexes $[UO_2(acetamidoxime)_4]$-$(NO_3)_2$ (1) and $[UO_2(benzamidoxime)_4](NO_3)_2 \cdot xS$ (S = nitromethane or 1,2-dichloroethane, x < 1) (2) were prepared by the reaction of uranyl nitrate with the corresponding amidoxime in ethanolic solution, and characterized by thermal analysis and infrared spectroscopy. The crystal structures of the acetamidoxime complex and the 1,2-dichloroethane-containing benzamidoxime complex (2a) were determined by single crystal X-ray diffraction measurements and refined to R_1 = 0.018 and 0.070, respectively. 1 crystallizes in the monoclinic space group I2/c with a = 14.929(3), b = 8.946(2), c = 16.790(4) Å, β = 96.01(2)° and Z = 4, whereas crystals of 2a are triclinic, space group $P\bar{1}$ with a = 9.890(4), b = 14.226(6), c = 15.227(6) Å, α = 75.76(3), β = 87.13(3), γ = 81.22(3)° and Z = 2. In both complexes the linear uranyl group is equatorially surrounded by four oxygen atoms of monodentate amidoxime ligands, the mean bond lengths in 1 and 2a being: $U-O_{uranyl}$ = 1.775 and 1.78 Å and $U-O_{amidoxime}$ = 2.308 and 2.26 Å, respectively. In accordance with infrared spectroscopic results the nitrate ions are not coordinated to uranium, but interact with the ligand molecules via hydrogen bonds.

Introduction

Our studies on the extraction of uranium from seawater revealed hydroxylamine derivatives of poly-(acrylonitriles), so-called poly(acrylamidoximes), to be capable of accumulating uranium from natural seawater by more than 3600 ppm at the natural pH of 8.1–8.3 [1–3]. With regard to loading capacity and uranium selectivity, these resins are superior to hydrous titanium oxide [4], the hitherto most promising sorbent for the recovery of uranium from seawater [5]. Beside cyclic imidoxime groups, open-chain amidoxime groups $-C\begin{smallmatrix}\nearrow NOH \\ \searrow NH_2\end{smallmatrix}$ were shown to

be mainly bound to the polymeric framework. For this reason we were interested in studying the complexing behaviour of the amidoxime functional group toward uranyl ions, in particular the coordination symmetry and the kind of donor atoms in monomeric uranyl amidoxime model complexes.

Amidoximes [6, 7], imide monoximes [8] and imide dioximes [9, 10] form coloured complexes with uranyl ions in solution. Benzamidoxime [11], salicyl-amidoxime [12] and nicotinamidoxime [13], which are reported to compose 1:1 complexes with UO_2^{2+} in solution, have been used as reagents for the analytical determination of uranium. Uranyl complexes of o-methylbenzamidoxime [14] and benzanilidoxime [15] have been studied in solution and the compounds $[UO_2(C_6H_5 \cdot NH \cdot C(C_6H_5):NO)_2]$ [15] and $[UO_2(OH)(HONH \cdot CO \cdot CH_2 \cdot C(NH_2):NO)]$ [16] are known to exist in the solid state.

X-ray structure analyses of Co(II), Co(III), Ni(II), Cu(II), Pb(II) and Pt(II) complexes of amidoximes revealed the oxime nitrogen to be coordinated to the metal atom [17–23], but also the existence of five-membered chelate rings of Ni(II) with O,N'-coordinated benzamidoximate [24] and of Mo(VI) with N-hydroxy-N-methylacetamidinate [25] has been established by X-ray diffraction.

We have prepared and isolated for the first time cationic uranyl complexes of acetamidoxime and benzamidoxime [26] which have been characterized by thermal analysis, infrared spectroscopy, and single crystal X-ray structure determinations. To our knowledge these are the first reported crystal structure analyses of amidoxime uranyl complexes.

Experimental

Preparation of the Ligands

Acetamidoxime and benzamidoxime were obtained from acetonitrile and benzonitrile, respectively, by reaction with butanolic or aqueous ethanolic

hydroxylamine solutions according to standard methods [27, 28]. Acetamidoxime, m.p.: 138 °C [29]; benzamidoxime, m.p.: 79 °C.

Preparation of [UO₂(acetamidoxime)₄](NO₃)₂

A solution of 2.0 g (4 mmol) $UO_2(NO_3)_2 \cdot 6H_2O$ in 100 ml ethanol was added to a stirred solution of 3.0 g (40 mmol) acetamidoxime in 200 ml ethanol at 50 °C. The reaction mixture was treated with 900 ml diethyl ether, resulting in the precipitation of a yellow complex which was collected by filtration, washed, and dried under vacuum. Yield: 2.6 g (93%). The microcrystalline product is easily soluble in water, methanol, and ethanol but insoluble in methylene chloride. Recrystallization from nitromethane yielded yellow needles, m.p. 191 °C. *Anal.* Calcd. for $C_8H_{24}N_{10}O_{12}U$: C, 13.92; H, 3.50; N, 20.29; U, 34.48. Found: C, 13.88; H, 3.56; N, 20.36; U, 33.91. Crystals suitable for structure determination were grown from a methanol/nitromethane solution (1:8 v/v) by slow evaporation over a molecular sieve (5 Å).

Preparation of [UO₂(benzamidoxime)₄](NO₃)₂·xS (S = nitromethane or 1,2-dichloroethane)

Solutions containing 1.5 g (3 mmol) $UO_2(NO_3)_2 \cdot 6H_2O$ in 5 ml ethanol and 1.7 g (12 mmol) benzamidoxime in 10 ml ethanol were mixed and heated at 50 °C. After evaporation to dryness the residue was dissolved in hot nitromethane and left for crystallization, yielding 2.6 g (90%) of an orange-yellow complex, m.p. 87–89 °C. *Anal.* Calcd. for $[UO_2(C_7H_8N_2O)_4](NO_3)_2 \cdot 0.4CH_3NO_2$: C, 35.42; H, 3.47; N, 15.31; U, 24.72. Found: C, 35.70; H, 3.54; N, 15.05; U, 25.36. The crystals were readily soluble in water, methanol and acetone but almost insoluble in methylene chloride. Recrystallization from a nitromethane/1,2-dichloroethane solution (1:5 v/v) by slow evaporation over molecular sieve (5 Å) resulted in yellow needle-shaped crystals suitable for X-ray structure determination, m.p. 110–115 °C. *Anal.* Calcd. for $[UO_2(C_7H_8N_2O)_4](NO_3)_2 \cdot 0.4C_2H_4Cl_2$: C, 35.36; H, 3.46; N, 14.32. Found: C, 35.10; H, 3.43; N, 14.19.

IR Spectra and Thermal Analysis

Infrared spectra (400–4000 cm^{-1}) were recorded on a Perkin-Elmer 225 spectrophotometer using KBr pellets and nujol mulls. Simultaneous thermogravimetry and differential thermal analysis were carried out with a Netzsch thermoanalyzer, model STA 429. The samples (about 50 mg) were heated at a rate of 1 K min^{-1} in a dynamic nitrogen atmosphere.

X-Ray Data Collection and Reduction

Single crystals of *1* and *2a* were used for the X-ray measurements. X-ray intensity data were collected at −133 °C on a Syntex P2₁ four circle diffractometer equipped with a graphite monochromator and a scintillation counter. The unit cell parameters were obtained by least-squares refinements of the setting angles of 15 high-order reflections. They are given in Table I, together with relevant information concerning experimental conditions and details of the

TABLE I. Details of Data Collection and Structure Refinements for *1* and *2a*.

	1	*2a*
a, Å	14.929(3)	9.890(4)
b, Å	8.946(2)	14.226(6)
c, Å	16.790(4)	15.227(6)
α, °		75.76(3)
β, °	96.01(2)	87.13(3)
γ, °		81.22(3)
V, Å³	2230.1	2052.0
Space group	I2/c	P1̄
Z	4	2
d_{calc}, g cm⁻³	2.056	1.679
Temperature, °C	−133	−133
Cryst. dimension, mm	0.150 × 0.750 × 0.186	0.5 × 0.2 × 0.2
μ(MoKα), cm⁻¹	69.7	65.1
Radiation	MoKα	MoKα
Scan speed (intensity depending), °min⁻¹	4–30	4–30
(sin θ)/λ cutoff, Å⁻¹	0.64	0.54
Scan mode	2θ−θ	2θ−θ
Total number of independent reflexions	2227	5392
Reflexions used (in parentheses: rejection criterion)	1868 (I < 2σ(I))	4368 (I < 2σ(I))
Number of variables	190	405
R₁, R₂	0.018, 0.025	0.070, 0.071

structure solutions and refinements. The intensities of both data sets were corrected for absorption. In the case of *1* a numerical method based on the Gaussian integration procedure was applied, whereas in the case of *2a* an empirical correction (ψ-scan) was performed. In the final steps of the data reduction Lorentz and polarization factor corrections were applied.

The variance of I was calculated as $\sigma(I)^2 = S + (B_1 + B_2)(t_S/2t_B)^2$ where S, B_1 and B_2 are the scan and individual background counts respectively and t_S and t_B are their counting times.

Solutions and Refinements of the Structures

All calculations, including those of the data reduction steps, were performed using programs of the Syntex EXTL and SHELXTL program packages. The positions of the uranium atoms as starting points for the solutions of both structures were derived from Patterson syntheses. Repeated least-squares refinements followed by difference Fourier syntheses revealed the positions of all atoms in the unit cell of *1*. Due to slight distortions as a consequence of disordered benzamidoxime and nitrate residues, the H atoms in the structure of *2a* could not be directly located. Their contributions to the structure factors were neglected in the refinement procedures.

Final full-matrix least-squares refinement cycles using anisotropic temperature factors for most of the non-hydrogen atoms and isotropic temperature factors for the remaining ones converged to $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o| = 0.018$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2} = 0.025$ for *1* and $R_1 = 0.070$ and $R_2 = 0.071$ for *2a*, respectively. The function minimized was $R = \Sigma w(|F_o| - |F_c|)^2$, w being defined as $w = [\sigma^2(F_o) + (0.01F_o)^2]^{-1}$ with $\sigma(F_o) = \sigma(I) \cdot Lp^{-1}/2F_o$. Atomic scattering factors for spherical neutral free atoms (all except H) or bonded (H) atoms, as well as anomalous scattering contributions, were taken from the International Tables [30].

The final positional and thermal parameters with standard deviations for *1* and *2a* are summarized in Tables II and III. The phenyl group of the disordered benzamidoxime ligand in the structure of *2a* is represented in Table III by calculated C atoms that define an ideal hexagon. The atomic labelling schemes for the cations of *1* and *2a* are given in Figs. 1 and 2. Stereoscopic projections of the cations with thermal ellipsoids (50% probability) of all non-hydrogen atoms of *1* and the U and O atoms of *2a* (other atoms: arbitrary circles) are displayed in Figs. 3 and 4, respectively.

Results and Discussion

The reaction of uranyl nitrate with a 10-molar excess of acetamidoxime or a 4-molar excess of
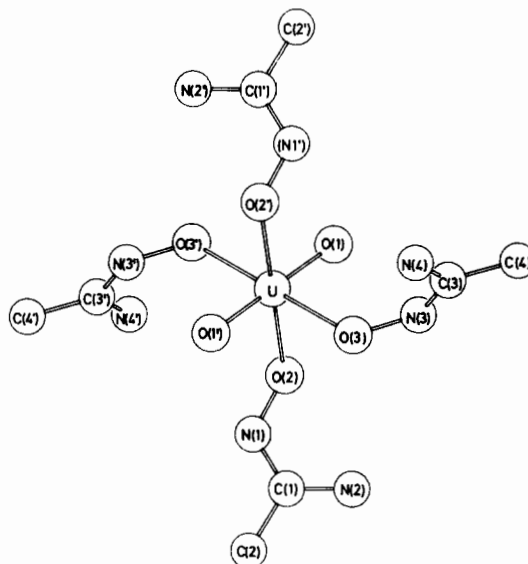

Fig. 1. Projection of the $[UO_2(\text{acetamidoxime})_4]^{2+}$ cation, with the atomic labelling scheme.

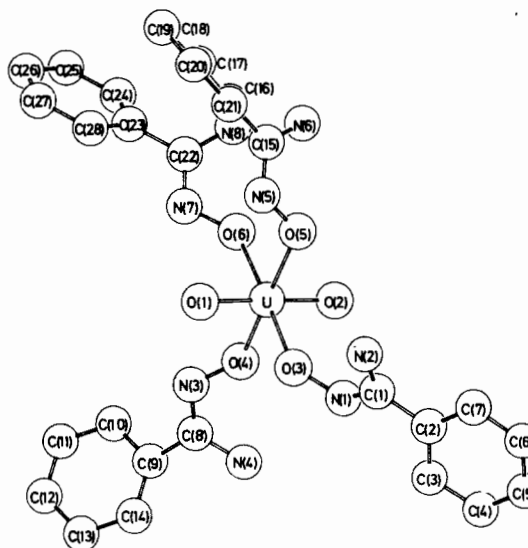

Fig. 2. Projection of the $[UO_2(\text{benzamidoxime})_4]^{2+}$ cation, with the atomic labelling scheme.

benzamidoxime led to the formation of crystalline uranyl complexes showing a molar ratio U: amidoxime of 1:4, as indicated by elemental analysis. In contrast to $[UO_2(\text{acetamidoxime})_4](NO_3)_2$, the benzamidoxime complex $[UO_2(\text{benzamidoxime})_4](NO_3)_2 \cdot xS$ was found to contain non-stoichiometric amounts of the solvents when crystallized from nitromethane ($S = CH_3NO_2$) or nitromethane/1,2-dichloroethane ($S = C_2H_4Cl_2$) solutions. In Fig. 5 the thermoanalytical curves of the complex compounds are represented. The decomposition of the acetamidoxime complex starts at about 150 °C and is accompanied

TABLE II. Positional and Thermal Parameters of $[UO_2(acetamidoxime)_4](NO_3)_2$ (I). [a]

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
U	0.0	0.0	0.0	0.832(8)	0.785(8)	0.859(8)	−0.067(6)	0.142(5)	−0.048(5)
O(1)	0.0453(2)	0.1665(3)	0.0455(1)	1.6(1)	1.1(1)	1.4(1)	−0.4(1)	0.0(1)	−0.3(1)
O(2)	−0.1195(2)	0.0071(2)	0.0760(2)	1.5(1)	1.5(1)	1.0(1)	−0.1(1)	0.4(1)	−0.3(1)
O(3)	0.0818(2)	−0.1358(3)	0.0999(1)	1.3(1)	1.0(1)	1.3(1)	0.2(1)	0.0(1)	0.0(1)
O(4)[b]	0.4049(2)	−0.1504(3)	0.1315(2)	1.7(1)	1.3(1)	4.5(2)	0.3(1)	1.0(1)	0.3(1)
O(5)[b]	0.2957(3)	0.0077(3)	0.1361(3)	1.8(1)	2.4(2)	7.1(3)	0.4(1)	1.4(2)	−0.7(1)
O(6)[b]	0.4278(2)	0.0853(3)	0.1158(2)	2.6(1)	1.2(1)	5.2(2)	−0.4(1)	1.6(1)	−0.2(1)
N(1)	−0.1246(2)	0.1107(4)	0.1351(2)	1.4(1)	1.0(1)	1.4(1)	0.0(1)	0.4(1)	0.0(1)
N(2)	−0.1211(3)	−0.0710(4)	0.2306(2)	2.9(2)	1.9(2)	1.1(1)	0.1(1)	0.2(1)	0.2(1)
N(3)	0.0793(2)	−0.2901(3)	0.0950(2)	1.1(1)	1.0(1)	2.0(1)	−0.2(1)	0.1(1)	0.2(1)
N(4)	0.2267(2)	−0.2928(4)	0.0702(2)	1.1(1)	1.3(1)	3.2(2)	0.0(1)	0.4(1)	−0.1(1)
N(5)[b]	0.3760(3)	−0.0186(3)	0.1291(2)	1.7(1)	1.4(1)	2.7(2)	−0.1(1)	0.6(1)	−0.5(1)
C(1)	−0.1244(2)	0.0705(5)	0.2095(2)	0.9(1)	1.9(2)	1.3(1)	0.1(1)	0.2(1)	0.1(1)
C(2)	−0.1283(3)	0.1895(5)	0.2710(2)	2.0(2)	1.9(2)	1.6(2)	−0.2(1)	0.3(1)	−0.3(1)
C(3)	0.1506(2)	−0.3649(4)	0.0810(2)	1.3(1)	1.2(1)	1.2(1)	0.2(1)	0.0(1)	0.0(1)
C(4)	0.1468(3)	−0.5292(5)	0.0779(3)	2.1(2)	1.2(2)	2.9(2)	−0.1(1)	0.2(1)	0.2(1)
H(1)	−0.119(2)	0.190(4)	0.127(2)	0.6(8)					
H(2)	−0.113(3)	−0.144(5)	0.195(3)	2.5(10)					
H(3)	−0.114(3)	−0.082(6)	0.282(3)	3.0(11)					
H(4)	−0.146(3)	0.272(4)	0.246(2)	1.7(8)					
H(5)	−0.169(3)	0.154(5)	0.304(3)	3.7(11)					
H(6)	−0.069(3)	0.203(4)	0.306(2)	2.1(9)					
H(7)	0.028(3)	−0.332(5)	0.104(2)	2.6(10)					
H(8)	0.228(3)	−0.210(4)	0.074(2)	1.1(8)					
H(9)	0.290(3)	−0.373(5)	0.076(3)	4.1(11)					
H(10)	0.082(3)	−0.571(5)	0.068(2)	1.7(8)					
H(11)	0.177(2)	−0.565(4)	0.131(2)	1.1(8)					
H(12)	0.156(4)	−0.558(6)	0.020(3)	3.9(11)					

[a] The anisotropic temperature factor is defined as $\exp[-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. The B value of the isotropically refined atoms are given as B_{11}.   [b] Atom of the nitrate group.

TABLE III. Positional and Thermal Parameters of the $[UO_2(benzamidoxime)_4]^{2+}$ Cation of $2a$. [a]

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
U	0.23026(7)	0.07652(5)	0.45250(5)	1.70(3)	2.11(3)	2.77(3)	−0.04(2)	0.28(2)	−1.62(2)
O(1)	0.3875(11)	0.0719(7)	0.3892(7)	2.6(6)	1.9(5)	3.8(6)	−0.9(5)	0.3(5)	−0.5(5)
O(2)	0.0795(11)	0.0892(8)	0.5201(8)	2.3(6)	2.6(6)	5.0(7)	−0.9(5)	1.1(5)	−2.1(5)

Atom	x	y	z	U(11)	U(22)	U(33)	U(12)	U(13)	U(23)
O(3)	0.3497(10)	0.1292(7)	0.5531(7)	1.9(5)	2.5(5)	2.5(5)	-0.14(4)	0.2(4)	-1.0(5)
O(4)	0.1568(12)	0.2265(8)	0.3751(7)	4.8(7)	2.9(6)	1.9(6)	0.1(5)	-0.1(5)	0.2(5)
O(5)	0.2871(12)	-0.0837(8)	0.5307(8)	3.6(7)	2.1(5)	4.7(7)	0.0(5)	0.7(5)	-2.3(5)
O(6)	0.1299(12)	0.0182(9)	0.3520(8)	3.2(7)	5.7(8)	4.9(7)	-1.3(6)	0.7(6)	-4.3(6)
N(1)	0.2977(13)	0.1632(9)	0.6279(8)	2.4(7)	2.2(7)	1.4(4)	-0.4(5)	0.6(5)	-1.2(5)
N(2)	0.4244(14)	0.0278(9)	0.7178(8)	3.5(8)	2.1(7)	2.7(7)	1.4(6)	0.0(6)	-0.4(5)
N(3)	0.1946(18)	0.2885(11)	0.2978(11)	8.6(12)	1.9(7)	4.8(9)	2.9(8)	-0.4(9)	-0.3(7)
N(4)	0.1044(20)	0.4143(12)	0.3645(11)	10.2(14)	5.5(10)	5.0(10)	3.5(9)	0.1(9)	-3.7(8)
N(5)	0.3773(13)	-0.1513(9)	0.4987(8)	2.5(7)	1.5(6)	3.3(7)	-0.4(5)	0.4(6)	-0.9(5)
N(6)	0.1935(14)	-0.2355(10)	0.4975(11)	1.5(7)	3.2(8)	7.5(10)	-0.5(6)	0.0(7)	-2.7(7)
N(7)	0.1823(14)	-0.0057(10)	0.2733(9)	2.8(8)	4.0(8)	3.2(8)	-0.6(6)	0.3(6)	-2.6(7)
N(8)	0.0331(15)	-0.1211(11)	0.3016(9)	3.9(8)	5.7(9)	3.1(7)	-2.5(7)	1.8(7)	-2.5(7)
C(1)	0.3385(17)	0.1127(12)	0.7079(10)	3.0(9)	2.4(8)	1.6(8)	-0.4(7)	0.6(7)	-0.5(7)
C(2)	0.2929(16)	0.1505(12)	0.7892(11)	2.2(8)	2.7(9)	2.8(9)	0.3(7)	-0.1(7)	-1.3(7)
C(3)	0.2529(18)	0.2532(12)	0.7756(12)	3.8(10)	2.7(9)	4.1(10)	-0.9(8)	0.0(8)	-2.2(8)
C(4)	0.2090(20)	0.2857(14)	0.8561(12)	5.0(12)	4.6(11)	2.6(9)	-0.4(9)	0.7(8)	-1.9(9)
C(5)	0.2110(18)	0.2217(15)	0.9406(12)	2.5(9)	5.7(12)	2.6(9)	-0.2(8)	0.4(7)	-1.9(9)
C(6)	0.2527(17)	0.1220(14)	0.9509(11)	2.9(9)	4.1(10)	3.4(9)	-0.5(8)	0.3(7)	-1.7(8)
C(7)	0.2945(16)	0.0857(12)	0.8735(11)	2.0(8)	3.9(9)	2.1(8)	-0.3(7)	0.3(7)	-0.8(7)
C(8)	0.1582(25)	0.3809(19)	0.2926(17)	6.4(6)					
C(9)	0.1489	0.4646	0.2050						
C(10)	0.1309	0.4338	0.1268						
C(11)	0.1695	0.4884	0.0425						
C(12)	0.2260	0.5739	0.0365						
C(13)	0.2441	0.6047	0.1148						
C(14)	0.2055	0.5501	0.1990						
C(15)	0.3263(20)	-0.2253(12)	0.4841(12)	4.4(11)	1.9(8)	4.3(10)	0.4(8)	-0.6(9)	-1.5(8)
C(16)	0.4235(17)	-0.3024(11)	0.4521(13)	1.9(9)	1.5(8)	5.9(11)	-0.4(7)	1.2(8)	-0.9(8)
C(17)	0.3890(19)	-0.3320(12)	0.3762(13)	3.8(10)	2.7(9)	5.5(11)	-0.7(8)	1.7(9)	-2.1(8)
C(18)	0.4810(24)	-0.4023(16)	0.3417(16)	4.7(13)	4.5(12)	7.7(15)	-1.5(10)	1.8(11)	-1.3(11)
C(19)	0.6011(24)	-0.4430(14)	0.3917(18)	4.8(13)	2.8(10)	8.5(16)	-1.0(9)	3.2(12)	-2.6(11)
C(20)	0.6363(20)	-0.4153(13)	0.4673(17)	2.9(11)	2.5(10)	9.2(16)	-0.3(8)	2.3(11)	-0.5(10)
C(21)	0.5456(18)	-0.3418(12)	0.5002(14)	2.0(9)	1.3(8)	7.6(13)	-0.1(7)	0.7(9)	-0.4(8)
C(22)	0.1302(17)	-0.0750(12)	0.2512(11)	2.3(9)	3.7(9)	2.4(8)	-0.5(7)	0.1(7)	-2.3(7)
C(23)	0.1816(17)	-0.1042(11)	0.1657(11)	2.9(9)	1.6(8)	3.0(9)	-0.7(7)	0.9(7)	-1.0(7)
C(24)	0.0853(19)	-0.1093(12)	0.1043(12)	4.4(11)	3.6(9)	3.2(9)	-0.3(8)	-0.6(8)	-1.8(8)
C(25)	0.1315(20)	-0.1354(14)	0.0231(12)	4.1(11)	4.9(11)	3.3(10)	-0.2(9)	0.5(8)	-1.7(8)
C(26)	0.2753(20)	-0.1531(12)	0.0056(13)	4.3(11)	2.3(9)	5.1(11)	-0.9(8)	1.2(9)	-1.4(8)
C(27)	0.3692(20)	-0.1454(13)	0.0673(12)	4.3(11)	4.1(10)	3.5(10)	-0.9(9)	0.1(9)	-1.6(8)
C(28)	0.3220(17)	-0.1194(12)	0.1482(12)	2.1(9)	3.8(10)	4.1(10)	-0.6(7)	1.1(8)	-2.0(8)

[a] The temperature factors are defined as in Table II. The atoms C(9) to C(14) are calculated to define a regular hexagon (see text).
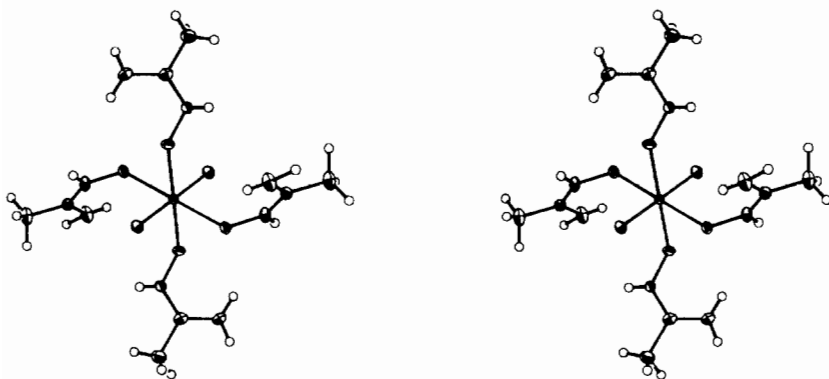
Fig. 3. Stereoscopic view of the $[UO_2(acetamidoxime)_4]^{2+}$ cation with thermal ellipsoids of the non-hydrogen atoms (50% probability level, $-133\ ^\circ C$).
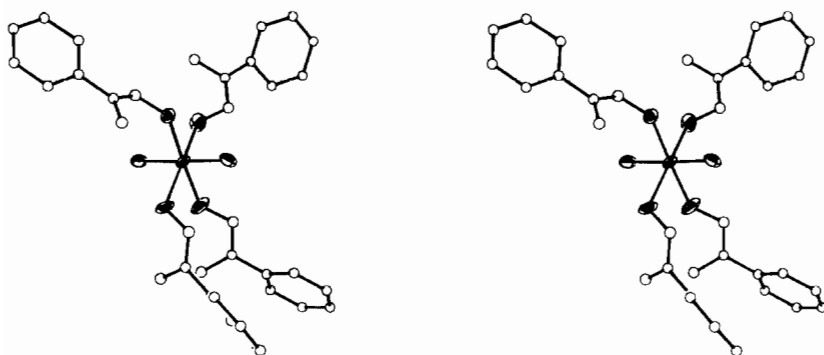

Fig. 4. Stereoscopic view of the $[UO_2(benzamidoxime)_4]^{2+}$ cation with thermal ellipsoids of the U and O atoms (50% probability level, $-133\ ^\circ C$).

by exothermic peaks at 180, 210 and 270 °C. No thermal effect is observed below 150 °C. The benzamidoxime complex, however, exhibits a decomposition step between 55 and 90 °C (TG 1 and 2) with an endothermic peak at 85 °C in the case of the nitromethane compound and a decomposition step between 70 and 105 °C (TG 2) with an endothermic peak at 95 °C in the case of 1,2-dichloro-ethane as constituent. The weight losses of 2.6 and 4.0% respectively correspond to 0.4 mol of solvent per mol of the benzamidoxime complex. After the evolution of the solvents the benzamidoxime complex starts to decompose exothermally at 125 °C and shows DTA peaks at 145, 180, 210, and 215 °C. An appreciable decrease of the solvent fraction x is observed during storage of the crystals, demonstrating that the solvent molecules are not held very strongly in the lattice.

The infrared spectra of both complexes *1* and *2* exhibit absorptions which can be assigned to ionic nitrate groups. However, the band of the doubly degenerate stretching vibration of the free nitrate ion is split into strong absorptions at 1310 and 1383 cm^{-1}, indicating a symmetry of the nitrate lower

than D_{3h}. A comparable splitting is observed for the nitrate combination bands at 2420 and 2340 cm^{-1} of the acetamidoxime complex. This separation is smaller than for uranyl complexes containing unidentate or bidentate nitrate groups [31, 32] but similar to the splitting of 80 cm^{-1} reported for the complex $[UO_2(urea)_4(H_2O)](NO_3)_2$ [33], the nitrato groups of which are not coordinated to the uranyl ion but involved in an extensive system of hydrogen bonds, as demonstrated by a neutron diffraction study [34]. Obviously, the interaction of the nitrate ions with the acetamidoxime and benzamidoxime ligands via hydrogen bonds gives rise to their reduced symmetry in the uranyl complexes.

Strong bands at 1577 cm^{-1} of *1* and 1653 cm^{-1} of *2* are attributed to the C=N stretching mode of the amidoxime ligands. In free acetamidoxime and benz-amidoxime these bands occur at 1656 and 1650 cm^{-1}, respectively. The high frequency shift in the case of acetamidoxime can be associated with proto-nation or the oximic nitrogen on complexation, in accordance with assignments made for the band near 1690 cm^{-1} in the hydrochlorides of substituted acetamidoximes [35]. The asymmetric stretching
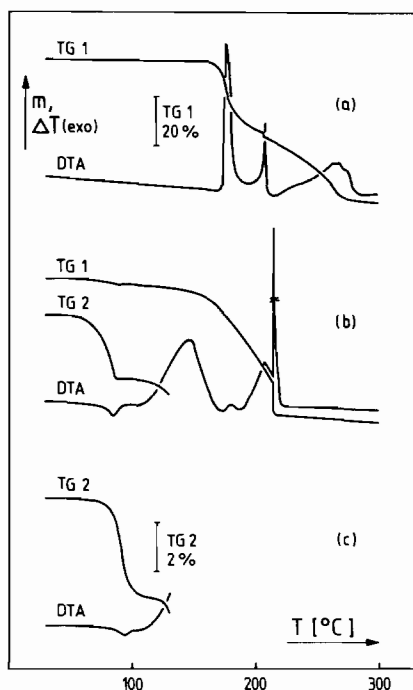
Fig. 5. TG and DTA curves of the complexes [UO₂(acetamid-oxime)₄](NO₃)₂ (a), [UO₂(benzamidoxime)₄](NO₃)₂·0.4-CH₃NO₂ (b), and [UO₂(benzamidoxime)₄](NO₃)₂· 0.4C₂H₄-Cl₂ (c). The recording sensitivity of TG 2 is 10 times that of TG 1.

TABLE IV. Selected Bond Lengths [Å] of the [UO₂(ace-tamidoxime)₄]²⁺ and [UO₂(benzamidoxime)₄]²⁺ Cations of *1* and *2a*.

$[UO_2(acetamidoxime)_4]^{2+}$		$[UO_2(benzamidoxime)_4]^{2+}$	
U–O(1)	1.775(2)	U–O(1)	1.789(11)
U–O(2)	2.301(3)	U–O(2)	1.773(11)
U–O(3)	2.313(2)	U–O(3)	2.305(10)
		U–O(4)	2.201(12)
		U–O(5)	2.296(11)
		U–O(6)	2.247(12)
N(1)–O(2)	1.366(4)	N(1)–O(3)	1.39(2)
N(3)–O(3)	1.383(4)	N(3)–O(4)	1.36(2)
C(1)–N(1)	1.300(5)	N(5)–O(5)	1.37(2)
C(1)–N(2)	1.314(5)	N(7)–O(6)	1.38(2)
C(3)–N(3)	1.299(5)	C(1)–N(1)	1.30(2)
C(3)–N(4)	1.335(5)	C(1)–N(2)	1.35(2)
C(1)–C(2)	1.488(6)	C(8)–N(3)	1.29(3)
C(3)–C(4)	1.472(5)	C(8)–N(4)	1.35(3)
		C(15)–N(5)	1.30(2)
		C(15)–N(6)	1.34(2)
		C(22)–N(7)	1.30(2)
		C(22)–N(8)	1.35(2)
		C(1)–C(2)	1.49(2)
		C(15)–C(16)	1.50(3)
		C(22)–C(23)	1.50(2)

vibration of the UO₂ group is observed as a strong band at 915 and 887 cm⁻¹ in the spectra of *1* and *2*, respectively. The spectra of *2* differ only in the appearance of characteristic absorptions of nitro-methane (1550 cm⁻¹) and 1,2-dichloroethane (710 cm⁻¹).

The crystal structures of *1* and *2a* display discrete [UO₂(ligand)₄]²⁺ cations, nitrate ions which are not coordinated to uranyl, and in the case of the benzamidoxime complex 1,2-dichloroethane molecules. The uranium atoms are approximately square-bipyramidally surrounded by four oxygen atoms of the monodentate amidoxime groups and the two oxygen atoms of the uranyl group as axial ligands (see Figs. 3 and 4). In the acetamidoxime complex, the ligand molecules exist as zwitterions with deprotonated oxygen and protonated oxime nitrogen. For the benzamidoxime complex the same bonding of H atoms in the ligands can be assumed, but could not be established unambiguously with respect to the lower precision of the X-ray diffraction data. A similar zwitterionic arrangement of monodentate hydroxylamine ligands with coordinated oxygen has been reported for the uranyl complex [UO₂(NH₂O)₂-(NH₃O)₂]·2H₂O, the structure of which was solved by neutron diffraction [36].

Bond distances and angles of the amidoxime complexes are given in Tables IV and V, respectively. The

uranyl group turns out to be linear and perpendicular to the equatorial plane of the amidoxime oxygen atoms in both complexes. The U–O distances of 1.775(2) and 1.78 Å (mean values) of the uranyl groups in *1* and *2a*, respectively, are in the expected range. The average equatorial U–O bond lengths, which in contrast to the uranyl bond length clearly depends on the equatorial coordination number [37–39], are 2.307 and 2.26 Å, respectively. The bond lengths agree well with those reported for other uranyl complexes having four oxygen atoms in the equatorial plane [40–45], and are significantly shorter than the U–O bond lengths of the more common pentacoordinate uranyl complexes with five equatorially-arranged oxygen donor atoms (average 2.38 Å) [39, 46, 47].

The amidoxime groups are planar in both complexes (within experimental errors). The ligand molecules occur in the Z-configuration about the C=N$_{oxime}$ bond, the thermodynamically stable configuration of free N'-unsubstituted amidoximes [48–51], in which the amido group is *cis*-located to the oxygen atom.

The C–N$_{oxime}$ distances in *1* and *2a* (average 1.299 and 1.30 Å, respectively) and the C–N$_{amide}$ distances (average 1.325 and 1.35 Å, respectively) are similar and are between those expected for carbon–nitrogen double and single bonds [52]. This result may be explained by delocalisation of electrons in the planar amidoxime system, as has been suggested

TABLE V. Selected Bond Angles [°] of the $[UO_2(acetamidoxime)_4]^{2+}$ and $[UO_2(benzamidoxime)_4]^{2+}$ Cations of *1* and *2a*.

$[UO_2(acetamidoxime)_4]^{2+a}$		$[UO_2(benzamidoxime)_4]^{2+}$	
O(1)–U–O(1')	180	O(1)–U–O(2)	176.7(5)
O(1)–U–O(2)	91.19(10)	O(1)–U–O(3)	85.3(4)
O(1)–U–O(2')	88.81(10)	O(1)–U–O(4)	92.4(5)
O(1)–U–O(3)	88.90(10)	O(1)–U–O(5)	91.2(4)
O(1)–U–O(3')	91.10(10)	O(1)–U–O(6)	90.7(5)
O(2)–U–O(2')	180	O(2)–U–O(3)	91.4(4)
O(2)–U–O(3)	89.64(8)	O(2)–U–O(4)	88.0(5)
O(2)–U–O(3')	90.36(8)	O(2)–U–O(5)	88.6(5)
O(3)–U–O(3')	180	O(2)–U–O(6)	92.6(5)
N(1)–O(2)–U	121.8(2)	O(3)–U–O(4)	93.4(4)
N(3)–O(3)–U	118.2(2)	O(3)–U–O(5)	91.0(4)
O(2)–N(1)–C(1)	121.1(3)	O(3)–U–O(6)	175.4(4)
O(3)–N(3)–C(3)	120.5(3)	O(4)–U–O(5)	174.5(4)
N(1)–C(1)–N(2)	121.5(4)	O(4)–U–O(6)	89.2(4)
N(2)–C(1)–C(2)	120.4(3)	O(5)–U–O(6)	86.7(4)
C(2)–C(1)–N(1)	118.2(3)	N(1)–O(3)–U	127.4(8)
N(3)–C(3)–N(4)	120.1(3)	N(3)–O(4)–U	136.4(9)
N(4)–C(3)–C(4)	120.5(3)	N(5)–O(5)–U	123.8(9)
C(4)–C(3)–N(3)	119.4(3)	N(7)–O(6)–U	129.7(9)
		O(3)–N(1)–C(1)	118(1)
		O(4)–N(3)–C(8)	116(2)
		O(5)–N(5)–C(15)	116(1)
		O(6)–N(7)–C(22)	115(1)
		N(1)–C(1)–N(2)	121(1)
		N(2)–C(1)–C(2)	120(1)
		C(2)–C(1)–N(1)	120(1)
		N(3)–C(8)–N(4)	122(2)
		N(5)–C(15)–N(6)	123(2)
		N(6)–C(15)–C(16)	120(2)
		C(16)–C(15)–N(5)	117(2)
		N(7)–C(22)–N(8)	123(2)
		N(8)–C(22)–C(23)	119(2)
		C(23)–C(22)–N(7)	118(2)

[a] Symmetry transformation for the primed atoms: $-x, -y, -z$.

for other amidoximes and amidoxime complexes [19, 24, 52–54]. The N–O bonds in both complexes (average 1.374 and 1.38 Å, respectively) are somewhat shorter than those usually found for free amidoximes (1.41–1.44 Å), but are similar to those reported for some N_{oxime}-coordinate oxamidoxime complexes [20, 55, 56].

In free amidoximes the bond angle C–N–O has been found to vary between 109 and 113° [49–54, 57–61]. In the acetamidoxime and benzamidoxime uranyl complexes the average C–N–O angles are 120.8 and 116°, respectively. This increase may be explained by the protonation of the oxime nitrogen. On complexation of this nitrogen atom C–N–O angles up to 121° have been observed [24, 53, 56].

The nitrate ions are not coordinated to the uranium atom in both complexes, but are involved in a system of hydrogen bonds. As in the case of $[UO_2$-$(urea)_4(H_2O)](NO_3)_2$ [34], the deviation of the nitrate ions from D_{3h} symmetry is not as large as for

bidentate nitrato groups. In the acetamidoxime complex the average N–O distance was found to be 1.246 Å with none of the individual values differing by more than three σ from the average. The individual O–N–O angles differ only slightly from 120°.

In the structure of *1* each oxygen atom of the nitrate ion is bonded to oxime or amide nitrogen atoms via hydrogen bonds. Though the H atoms in the structure of *2a* could not be located, short interionic $O_{nitrate} \ldots N_{oxime}$ contacts indicate similar hydrogen bonds.

In conclusion, the study points out that the uranyl ions in the amidoxime complexes investigated are coordinated by the oxygen atoms of the monodentate amidoxime ligands. On complexation a zwitterionic arrangement of the oxime groups is achieved, resulting in a high base strength of the oxygen donor atoms which form strong bonds to the typical 'hard' Lewis acid UO_2^{2+}. The equatorial coordination

number 4, found in both amidoxime complexes, is uncommon in crystals of uranyl complexes with organic ligands [40, 62–65].

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