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Transition Metal Complexes with the Thiosemicarbazide-based Ligands Part X. The Complexes of UO_2(II) with *S*-Methyl-1,4-bis(salicylidene)-isothiosemicarbazide (H_2L): [UO_2(L)A] (A = MeOH, EtOH, DMF). Crystal Structure of [UO_2(L)DMF]

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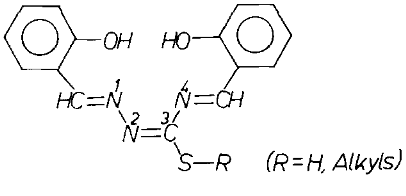
Abstract

The complexes of general formula [UO_2(L)A] (L = the dianion of quadridentate ONNO ligand *S*-methyl-1,4-bis(salicylidene)isothiosemicarbazide; A = MeOH, EtOH, DMF) were synthesized. The complexes containing MeOH and EtOH were obtained by the reaction of $UO_2(OAc)_2 \cdot 2H_2O$ with salicylaldehyde *S*-methylisothiosemicarbazone and salicylaldehyde in MeOH and EtOH, respectively, while the complex containing DMF was synthesized by recrystallization of the MeOH complex from DMF. [UO_2(L)DMF] crystallizes in the monoclinic space group $P2_1/c$ with cell constants: $a = 11.937(4)$, $b = 14.514(4)$, $c = 13.008(5)$ Å, $\beta = 104.93(2)°$, $V = 2178(1)$ Å^3; $M_r = 654.48$, $Z = 4$, $D_m = 2.00$, $D_c = 1.996$ g cm^{-3}.

The final R value for 1134 observed reflections is 0.043. The U coordination environment is a distorted pentagonal bipyramid with the uranyl O atoms [U–O 1.74(1) and 1.73(1) Å] in apical positions. The equatorial plane is defined by the two salicylaldehydate O atoms [U–O 2.20(2) and 2.27(2) Å], two isothiosemicarbazide N atoms [U–N 2.54(2) and 2.59(2) Å] from the chelate ligand and by the dimethylformamide O atom at 2.35(2) Å. The uranyl group is slightly bent [O–U–O 175.8(8)°] toward the N coordinated atoms. Presumably the alcohol complexes also have a pentagonal bipyramidal configuration.

Introduction

It has been shown [1, 2] that the ions VO(II), Ni(II), Cu(II) and Fe(III) in basic media represent convenient matrices for the condensation reaction of the terdentate ONS salicylaldehyde thiosemicarbazone (or its *S*-alkyl derivatives as an ONN ligand) with salicylaldehyde itself involving the N(4) atom, yielding thus a new quadridentate ONNO ligand.



The driving force of the process is the binding of the *in situ* formed ligand into a stable complex of the corresponding ion present in the solution. The demetallation reaction of the corresponding Ni(II) complex yielded the free ligand, which gave the possibility of preparing the complexes with those 3d-elements which do not take part in the above template reaction [3].

By preparing the complexes [UO_2(L)A] (L = dianion of the quadridentate ONNO ligand *S*-methyl-1,4-bis(salicylidene)isothiosemicarbazide; A = MeOH, EtOH, DMF) we have demonstrated that UO_2(II) can also play the role of a template in the condensation reaction of salicylaldehyde *S*-methylisothiosemicarbazone with salicylaldehyde.

Experimental

Preparation of the Complexes

[UO_2(L)MeOH]

The mixture of 1 mmol of $UO_2(CH_3COO)_2 \cdot 2H_2O$ and 1 mmol of salicylaldehyde *S*-methylisothiosemicarbazone [4] was dissolved by heating in 6 cm^3 of

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MeOH. After adding 0.5 cm^3 of salicylaldehyde the solution was heated mildly for about 5 min. The orange–red crystals formed during 12 h were filtered off and washed with MeOH and Et$_2$O. Yield: 0.45 g. *Anal.* Found: C, 32.80; H, 2.42; N, 6.72. Calc. for [UO$_2$(L)MeOH]: C, 33.28; H, 2.79; N, 6.85%.

[UO$_2$(L)EtOH]

This red complex was prepared in a similar way using absolute EtOH as solvent. Yield: 0.50 g. *Anal.* Found: C, 34.72; H, 3.16; N, 6.62. Calc. for [UO$_2$(L)EtOH]: C, 34.45; H, 3.05; N, 6.70%.

[UO$_2$(L)DMF]

Brown crystals used for the X-ray analysis were obtained by recrystallization of [UO$_2$(L)MeOH] from a hot MeOH + DMF (1:1) mixture. *Anal.* Found: C, 35.26; H, 3.63; N, 8.60. Calc. for [UO$_2$(L)DMF]: C, 34.84; H, 3.08; N, 8.56%.

Crystal Structure Determination

Crystal data for the [UO$_2$(L)MeOH] and [UO$_2$(L)EtOH] complexes were determined from oscillation and Weissenberg photographs. The first complex crystallizes in the triclinic $P\bar{1}$ (or $P1$) space group ($Z = 2$) with cell dimensions: $a = 9.88$, $b = 14.59$, $c = 8.16$ Å, $\alpha = 117.2$, $\beta = 102.7$, $\gamma = 88.6°$, $V = 1017$ Å^3; the second crystallizes in the orthorhombic *Pbca* space group ($Z = 8$) with cell dimensions: $a = 15.58$, $b = 11.86$, $c = 22.52$ Å, $V = 4161$ Å^3.

Crystals suitable for a complete X-ray structural analysis, although of poor quality, were only those of the [UO$_2$(L)DMF] complex. D_m was determined by flotation in a mixture of CCl$_4$ and CHBr$_3$. Intensity data were collected from a crystal of dimensions 0.20 × 0.14 × 0.17 mm on a Philips PW 1100 four-circle diffractometer using graphite monochromated Mo Kα radiation with the θ–2θ scanning technique, a scan width of 1.60° and a scan rate of 0.04° s^{-1}. Unit-cell parameters were obtained from least-squares refinement of 20 reflections within 2θ range of 11–21°. Only 1383 reflections appeared and were scanned within a quadrant $\pm h, k, l$ up to $(\sin\theta)/\lambda = 0.70$ Å^{-1}. Corrections were applied for Lorentz and polarization effects. A correction for absorption was also attempted (transmission factors were from 0.49 to 0.54), but no significant improvement was observed during the refinement. The U atom was located from the Patterson map and all non-H atoms from Fourier and Fourier-difference maps. H atoms were introduced in calculated positions. Full-matrix least-squares refinement on F was performed for 1134 unique reflections with $I > 3\sigma(I)$, using anisotropic thermal parameters for non-C and isotropic for C atoms, while parameters of H atoms were kept constant (176 parameters refined). The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F)$. At convergence the final $R(= R_w)$ was 0.043. Goodness-of-fit was 1.16 and parameters shifts were $<0.1\sigma$. Scattering and anomalous dispersion factors were taken from refs. 5–7. Calculations were performed mainly with XRAY76 [8] using the Univac 1110 computer at the University Computing Center in Zagreb.

Results and Discussion

The obtained complexes are crystalline substances, well soluble in DMF, Me$_2$CO, CHCl$_3$, C$_6$H$_6$, less soluble in MeOH, EtOH and Et$_2$O, and insoluble in H$_2$O. Their molar conductivities (*c.* 2 Ω^{-1} cm^2 mol^{-1}) suggest their non-electrolyte character. This feature arises from the fact that the chelate ligand is coordinated in its dianionic form, as in other transition metal complexes [1–3]. The X-ray analysis of [UO$_2$(L)DMF] confirms this circumstance.

Final atomic parameters for non-H atoms are listed in Table 1 and selected bond lengths and angles are reported in Table 2. Figure 1 shows an ORTEP

TABLE 1. Fractional positional parameters (×10^3; ×10^4 for U and S) for non-H atoms and equivalent isotropic temperature factors (defined as $(1/3)\Sigma_i\Sigma_j U_{ij}a_i a_j \vec{a}_i \vec{a}_j$) for non-C and isotropic temperature factors for C atoms (Å^2 × 10^2)

	x	y	z	U_{eq}/U
U	2055(1)	3733(1)	4705(1)	5.41(4)
S	4359(8)	4882(6)	2165(6)	10.0(4)
O(1)	87(1)	387(1)	361(1)	8.1(7)
O(2)	330(1)	363(1)	574(1)	7.5(7)
O(3)	83(1)	362(1)	585(1)	8.9(8)
O(2A)	170(2)	225(1)	477(2)	9.7(11)
O(2B)	195(1)	525(1)	511(1)	8.4(9)
N(1)	299(2)	290(1)	342(2)	5.9(9)
N(2)	354(2)	341(1)	274(2)	6.9(11)
N(3)	−33(2)	354(2)	696(2)	8.2(12)
N(4)	336(1)	469(1)	380(1)	5.3(8)
C(1)	469(2)	402(2)	133(2)	8.4(9)
C(2)	34(2)	398(2)	645(2)	6.6(8)
C(3)	370(2)	426(2)	298(2)	4.9(7)
C(4)	−51(3)	257(2)	680(2)	11.8(11)
C(5)	−86(3)	402(2)	764(2)	11.6(11)
C(1A)	252(2)	129(2)	364(2)	5.4(6)
C(2A)	193(2)	142(2)	442(2)	6.9(7)
C(3A)	158(2)	65(2)	490(2)	8.3(9)
C(4A)	173(3)	−23(2)	454(2)	11.0(11)
C(5A)	230(3)	−38(2)	380(2)	10.0(10)
C(6A)	272(2)	38(2)	331(2)	8.3(9)
C(7A)	298(2)	206(2)	317(2)	4.7(6)
C(1B)	351(2)	614(2)	483(2)	5.2(6)
C(2B)	259(2)	598(2)	531(2)	5.5(7)
C(3B)	233(2)	668(2)	601(2)	6.8(8)
C(4B)	301(2)	741(2)	621(2)	7.2(8)
C(5B)	391(2)	762(2)	573(2)	7.0(7)
C(6B)	415(2)	693(2)	506(2)	7.2(8)
C(7B)	381(2)	550(2)	409(2)	5.9(7)

TABLE 2. Selected bond lengths (A) and angles (°)

U–O(1)	1.74(1)	O(2B)–C(2B)	1.30(3)
U–O(2)	1.73(1)	N(1)–N(2)	1.44(3)
U–O(3)	2.35(2)	N(1)–C(7A)	1.27(3)
U–O(2A)	2.20(2)	N(2)–C(3)	1.27(3)
U–O(2B)	2.27(2)	N(3)–C(2)	1.33(4)
U–N(1)	2.54(2)	N(3)–C(4)	1.43(4)
U–N(4)	2.59(2)	N(3)–C(5)	1.39(4)
S–C(1)	1.77(3)	N(4)–C(7B)	1.30(3)
S–C(3)	1.74(3)	N(4)–C(3)	1.38(3)
O(3)–C(2)	1.20(3)	C(1A)–C(7A)	1.44(4)
O(2A)–C(2A)	1.34(3)	C(1B)–C(7B)	1.46(3)
O(1)–U–O(2)	175.8(8)	U–O(2A)–C(2A)	144(2)
O(1)–U–O(3)	91.0(7)	U–O(2B)–C(2B)	141(2)
O(1)–U–O(2A)	91.1(7)	U–N(1)–N(2)	121(1)
O(1)–U–O(2B)	89.6(7)	U–N(1)–C(7A)	131(2)
O(1)–U–N(1)	85.5(7)	N(1)–N(2)–C(3)	113(2)
O(1)–U–N(4)	91.5(7)	C(2)–N(3)–C(4)	119(2)
O(2)–U–O(3)	92.9(6)	C(2)–N(3)–C(5)	121(3)
O(2)–U–O(2A)	91.4(8)	C(4)–N(3)–C(5)	120(3)
O(2)–U–O(2B)	89.4(8)	U–N(4)–C(3)	116(1)
O(2)–U–N(1)	92.2(7)	U–N(4)–C(7B)	128(2)
O(2)–U–N(4)	84.4(7)	O(3)–C(2)–N(3)	125(2)
O(3)–U–O(2A)	75.6(7)	C(2A)–C(1A)–C(7A)	122(2)
O(3)–U–O(2B)	80.8(7)	O(2A)–C(2A)–C(1A)	123(3)
O(2A)–U–N(1)	71.4(7)	N(1)–C(7A)–C(1A)	128(2)
O(2B)–U–N(4)	70.1(7)	C(2B)–C(1B)–C(7B)	123(2)
N(1)–U–N(4)	62.5(6)	O(2B)–C(2B)–C(1B)	121(2)
C(1)–S–C(3)	102(1)	N(4)–C(7B)–C(1B)	127(2)
U–O(3)–C(2)	150(2)		

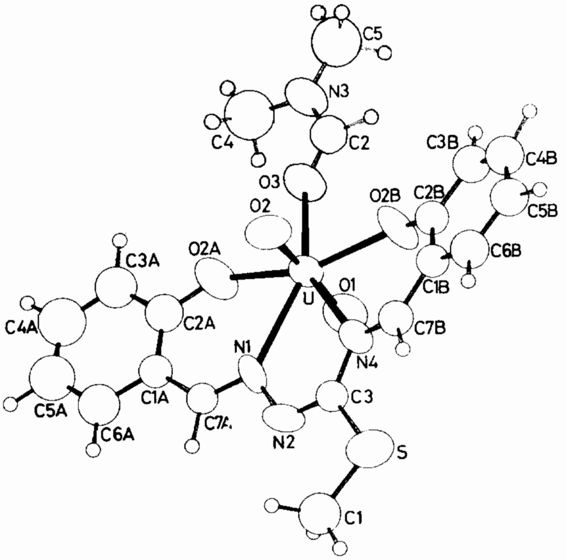

Fig. 1. Diagram showing the complex and atom numbering of the non-H atoms.

diagram [9] of the complex with the corresponding atom numbering.

The U coordination environment is a distorted pentagonal bipyramid. The pentagon in the equatorial plane is defined by the O(2A), O(2B), N(1) and N(4) atoms of the quadridentate ligand and by the O(3) atom from the DMF molecule (Fig. 1).

While U–O bond lengths of the uranyl group seem to be little affected by equatorially coordinated atoms [10], it is reported that its deviations from linearity could be dependent on contact distances between the uranyl O atoms and the equatorial atoms: the bending being in the direction to reduce steric repulsions between uranyl and salicylidene O atoms [11, 12] and being diminished as the minimal contact distances lengthen [13]. These findings are confirmed by this structure determination.

The bond lengths between the U atom and the equatorial O atoms [2.20(2), 2.27(2) Å] and N atoms [2.54(2), 2.59(2) Å] compare well with those reported for most of UO_2–bis(salicylidene) structures [10–17]. The U–O(3) bond length of 2.35(2) Å involving the O atom from the DMF molecule is slightly shorter than the U–O(DMF) bonds of 2.400(4) [18] and 2.45(2) Å [19], where UO_2^{2+} groups are also pentagonally coordinated.

The two wings of the ligand involving O(2A)–C(2A)...C(7A)–N(1) and O(2B)–C(2B)...C(7B)–N(4) atoms are inclined with each other by 27.4(4)°. They form dihedral angles of 6.9(4) and 21.0(4)°, respectively, with the equatorial plane. The pentagon defining the equatorial plane is rather puckered showing atom deviations from the plane within ±0.12(2) Å. The DMF molecule is planar within ±0.01(3) Å and forms a dihedral angle of 2.7(10)° with the equatorial plane. The U atom is practically within the equatorial and DMF planes with deviations of −0.007(2) and −0.006(2) Å respectively.

There is some electron delocalization in the isothiosemicarbazide bond lengths, as found in other 3d-metal complexes with this ligand [2, 20]. The methyl group at S and the N(4) atom are *trans* with respect to the C(3)–S bond, as expected taking into account the presence of the bulky substituent at N(4) (Fig. 1).

Intermolecular contact distances show that the molecular packing is accomplished by the usual van der Waals interactions.

The pentagonal bipyramidal configuration of $[UO_2(L)DMF]$ is in accord with the observation [16] that, in addition to a quadridentate Schiff base, a solvent molecule is usually coordinated in the uranyl equatorial plane [10, 14, 15]. In this way a similar coordination geometry can be assumed also for the $[UO_2(L)MeOH]$ and $[UO_2(L)EtOH]$ complexes. Coordination of MeOH and EtOH in these compounds is also supported by the circumstance that no significant loss in their masses is observed up to 190 °C.

Another indication that the above complexes are structurally similar is provided by the great similarity of their IR spectra, especially those of the MeOH and

EtOH adducts. The only significant differences in the IR spectra of the alcoholic complexes and those containing DMF are observed in the regions of high and medium frequencies. Thus, the IR spectra of the alcoholic complexes have in the region of 3600–3000 cm^{-1} one broad band of medium intensity which belongs to the ν(OH) of the alcohol. On the other hand, the IR spectrum of the DMF complex shows a very strong band at 1650 cm^{-1} corresponding to the ν(C=O) of the coordinated DMF. This band is located at 1675 cm^{-1} in the spectrum of DMF itself [21]. The characteristic bands of the UO_2^{2+} group in the spectra of all these complexes are observed at *c.* 900 (ν_a, very strong) and *c.* 800 (ν_s, weak) cm^{-1}, i.e. in the regions ($\nu_a = 950–870$ and $\nu_s = 885–780$ cm^{-1}) observed for the majority of dioxouranium(VI) complexes [22–26].

Supplementary Material

Tables of structure factors, anisotropic thermal parameters, mean planes, H atom parameters and non-essential bond lengths and angles are available from author N.G. on request.

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