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Three Coordination Modes of the Pentadentate Ligand 2,6-Diacetylpyridinedisemicarbazone

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Abstract

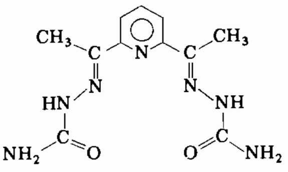
The pentadentate ligand 2,6-diacetylpyridinedisemicarbazone, DAPSC, reacts with $Cr(NO_3)_3 \cdot 9H_2O$ and forms two kinds of complexes. At pH = 3, the ligand is singly-deprotonated and crystals of $[Cr(DAPSC\text{-}H)(H_2O)_2](NO_3)_2 \cdot H_2O$ (**Ia**) are obtained. Evaporation of a solution at pH = 0, yields crystals of $[Cr(DAPSC)(H_2O)_2](NO_3)_3 \cdot 2H_2O$ (**II**) in which the ligand is fully protonated. The reaction of DAPSC with $UO_2(O_2CCH_3)_2$ in methanol, followed by crystallization of the product from DMSO yields crystals of $[UO_2(DAPSC\text{-}2H)(H_2O)] \cdot 2DMSO$ (**III**) in which the ligand is fully deprotonated. Compound **Ia** is monoclinic, space group $P2_1/n$ with $a = 11.746(1)$, $b = 14.752(2)$, $c = 11.866(1)$ Å, $\beta = 105.53(2)°$, $V = 1981(1)$ Å^3 and $Z = 4$. Compound **II** is monoclinic, space group, $P2_1/n$ with $a = 38.000(3)$, $b = 14.939(2)$, $c = 8.233(1)$ Å, $\beta = 96.12(2)°$, $V = 4647(1)$ Å^3 and $Z = 8$. Compound **III** is monoclinic, space group $P2_1/n$ with $a = 18.048(2)$, $b = 15.207(2)$, $c = 8.842(1)$ Å, $\beta = 97.72(2)°$, $V = 2405(1)$ Å^3 and $Z = 4$. The structures were refined using 2084, 4169 and 2516 reflections to R values of 4.4%, 7.8% and 4.8% respectively.

Introduction

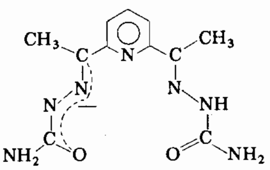
The formation of pentagonal-bipyramidal complexes of first-row transition elements and of In(III) with the pentadentate ligand 2,6-diacetylpyridinedisemicarbazone, DAPSC (**1**), was demonstrated by Palenik and coworkers [1–7]. The reaction of this ligand with $Cr(NO_3)_3 \cdot 9H_2O$ yielded a crystalline material which was subjected to an X-ray analysis and was formulated as '$[Cr(DAPSC)(H_2O)_2]^{3+}(NO_3^-)_2 \cdot OH^- \cdot H_2O$' (I). In this compound, which is the first example of a seven coordinated Cr(III) complex, the planar ligand (considered to be fully protonated) forms a pentagonal plane and two water ligands occupy the axial positions [1, 4].

A reexamination in our laboratory of this system revealed that the above formulation of compound **I** was mistaken. Our attention was drawn to this compound in the course of a reinvestigation of single crystal structures, in which the existence of a distinct hydroxide ion was claimed, particularly, in the hydrated form. The presence of an OH^- ion in **I**, rather than an H_2O molecule of crystallization was proposed in order to account for the mismatch of charges (3+ for the cation and 2− for the two nitrate counter-ions) [4]. The existence of such an OH^- ion in the above soluble chromium(III) compound implies that it should behave as a very strong base in aqueous solution. In preliminary experiments in our laboratory, it was found that aqueous solutions of **I** and of two other related compounds, '$[M(DAPSC)(H_2O)_2] \cdot (NO_3)_2 \cdot OH$' [M = Sc(III), In(III)] [6, 7] are not basic but acidic and therefore, the structures of these compounds merit a reexamination.

The authors of these reports [4, 6, 7] overlooked the possibility that the coordinated ligand DAPSC can be deprotonated and yield a half-conjugated mono anion, **2**, or a two-halves conjugated di-anion **3**.



1
DAPSC



2
DAPSC-H

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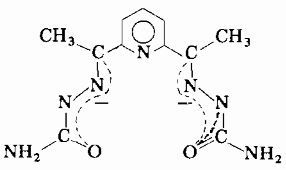

3
DAPSC-2H

A revision of this system in view of this concept may explain the mismatch of charges in all three 'hydroxide' compounds as well as the remarkable distortions in the geometry of these complexes.

We describe here the preparation and structural features of several compounds that demonstrate the bonding of metal atoms with **1**, **2** and **3**.

The compound $[Cr(DAPSC\text{-}H)(H_2O)_2](NO_3)_2 \cdot H_2O$ (**Ia**) is in fact, polymorphous with **I** and isostructural with the Sc(III) and In(III) compounds [6, 7]. In all these compounds, the ligand is in the singly-deprotonated form, 2, and the overall charge of the cation is 2+.

$[Cr(DAPSC)(H_2O)_2](NO_3)_3 \cdot 2H_2O$ (**II**) is obtained when **I** or **Ia** are recrystallized at low pH and contains the ligand in the fully-protonated form, DAPSC, **1**. And finally, in $[UO_2(DAPSC\text{-}2H)(H_2O)] \cdot 2DMSO$ (**III**) the ligand is in the doubly-deprotonated form, **3**, and the complex is therefore uncharged.

These results prove that the correct formulations of compound **I** and of the Sc(III) and In(III) complexes are: $[Cr(DAPSC\text{-}H)(H_2O)_2](NO_3)_2 \cdot 2H_2O$, $[Sc(DAPSC\text{-}H)(H_2O)_2](NO_3)_2 \cdot H_2O$ and $[In(DAPSC\text{-}H)(H_2O)_2](NO_3)_2 \cdot H_2O)$ respectively.

Experimental

Preparation of $[Cr(DAPSC\text{-}H)(H_2O)_2](NO_3)_2 \cdot H_2O$ *(Ia)*

The crude material was prepared following the procedure of Palenik *et al.* [4]. The recrystallization of the crude from water yields brown crystals of this compound as previously reported [4].

Preparation of $[Cr(DAPSC)(H_2O)_2](NO_3)_3 \cdot 2H_2O$ *(II)*

Recrystallization of the crude of **I** or **Ia** from 1 M HNO_3 yields yellow crystals of this compound.

Preparation of $[UO_2(DAPSC\text{-}2H)(H_2O) \cdot 2DMSO$ *(III)*

$UO_2(O_2CCH_3)_2 \cdot 2H_2O$ (0.155 g) was dissolved in methanol at 50 °C. DAPSC (0.1 g) was added and the solution was stirred for 1 h. A brown precipitate of $[UO_2(DAPSC\text{-}2H)MeOH]$ was obtained, collected and washed with methanol. *Anal.* Found: C, 25.05; H, 2.72; N, 17.23. Calc. for $C_{12}H_{17}N_7O_5U$: C, 25.00; H, 2.94; N, 17.01%. Recrystallization from DMSO in an open beaker yielded deep orange crystals of **III**.

X-ray Crystallography

Crystals of compounds **Ia** and **II** were sealed with epoxy cement to the end of a glass fiber. A crystal of **III** was mounted inside a glass capillary tube above a column of the solution from which it was grown.

Data were collected at 20 ± 2 °C on a Philips PW 1100 four-circle diffractometer. Mo Kα ($\lambda = 0.71069$ Å) radiation with a graphite crystal monochromator in the incident beam was used. The unit cell dimensions were obtained by a least-squares fit of 25 reflections in the range $12° < \theta < 16°$. Data were measured by using $\omega - 2\theta$ motion. Crystallographic data and other pertinent information are given in Table I. For each crystal Lorentz and polarization corrections were applied. Intensity data for **III** were corrected for absorption by the empirical ψ-scan method. The heavy atom positions in all structures were obtained by using the results of MULTAN direct method analysis. Structure **Ia** was refined in space group $P2_1/n$ to convergence by using anisotropic thermal parameters for all non-hydrogen atoms*. All the hydrogen atoms of the complex were located from the difference maps and were introduced in fixed positions using the riding model with $U = 0.05$. Structure **II** was refined in space group $P2_1/n$ to convergence using two blocks, one for Molecule 1, three NO_3^- groups and six water oxygens and a second block for Molecule 2 and three NO_3^- groups.

The oxygen atoms of one of the NO_3^- groups are disordered around N(18) between two positions in the ratio 2:3. The oxygen atoms O(58) through O(60) were refined with occupancy factor of 0.6 and O(61) through O(63) with occupancy factor of 0.4. Anisotropic thermal parameters were used for the chromium, oxygen and nitrogen atoms in the first coordination sphere and for all the NO_3^- oxygen atoms. Isotropic thermal parameters were used for the rest of the non-hydrogen atoms. Structure **III** was refined in space group $P2_1/n$ to convergence by using anisotropic thermal parameters for all non-hydrogen atoms.

The discrepancy indices $R = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2}$ are listed in Table I.

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*All crystallographic computing was done on CYBER 74 and CYBER 855 Computers at the Hebrew University of Jerusalem, using the SHELX 1977 structure determination package.

TABLE I. Crystallographic Data

Compound	**Ia**	**II**	**III**
Formula	$C_{11}H_{20}N_9O_{11}Cr$	$C_{11}H_{23}N_{10}O_{15}Cr$	$C_{15}H_{27}N_7O_7S_2U$
Formula weight	506.32	587.35	719.58
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	11.746(1)	38.000(3)	18.048(2)
b (Å)	14.752(2)	14.939(2)	15.207(2)
c (Å)	11.866(1)	8.233(1)	8.842(1)
β (°)	105.53(2)	96.12(2)	97.72(2)
V (Å^3)	1981(1)	4647(1)	2405(1)
Z	4	8	4
D_{calc} (g cm^{-3})	1.698	1.679	1.987
μ (cm^{-1})	5.96	5.27	66.47
Crystal size (mm)	0.1 × 0.1 × 0.15	0.15 × 0.15 × 0.2	0.1 × 0.15 × 0.15
Range of 2θ (°)	3–45	3–45	3–46
No. of unique data	2723	5924	3291
Data with $F_o^2 > 3\sigma(F_o^2)$	2084	4169	2516
No. of parameters	295	464	290
R	0.044	0.078	0.048
R_w	0.046	0.083	0.055

Results and Discussion

[Cr(DAPSC-H)(H$_2$O)$_2$](NO$_3$)$_2$·H$_2$O (Ia)

The structure and the dimensions of the cation in this compound are essentially identical with those found in **I** by Palenik *et al.* [4]. Therefore, see 'Supplementary Material' for the crystallographic data. (Some bond distances are included in Table VI for comparison.) The crystal consists of the distorted pentagonal-bipyramidal $[Cr(DAPSC\text{-}H)(H_2O)_2]^{2+}$ ion, hydrogen bonded to NO_3^- anions and the water molecule of crystallization. Since all the hydrogen atoms of the complex were located in this structure it is obvious from the hydrogen bonding scheme that one of the semi-carbazone NH groups is deprotonated. This nitrogen atom serves as an acceptor in a hydrogen bond with one of the H_2O ligands of a neighbouring complex (N···O distance of 2.69 Å). The negative charge on one section of the ligand is the main cause of the distortion of the system as will be discussed later. The H_2O molecule of crystallization is hydrogen bonded to one of the H_2O ligands of the complex (serves as an acceptor with OL–O(4) distance of 2.71 Å) and to the two NO_3^- anions (serves as a donor) with $HO(H)\cdots ONO_2$ distances of 2.91 and 2.95 Å.

[Cr(DAPSC)(H$_2$O)$_2$](NO$_3$)$_3$·2H$_2$O (II)

With eight molecules in the unit cell of space group $P2_1/n$ there are two molecules in the asymmetric unit, and no crystallographic symmetry is imposed upon either one. The atomic positional parameters are listed in Table II. Table III presents the important bond lengths and angles of Molecule 1. Figure 1 shows the numbering scheme in Molecule 1. The dimensions of the two molecules in the asymmetric unit are essentially identical, therefore for bond lengths and angles of Molecule 2 see 'Supplementary Material'. (Some important structural parameters of Molecules 1 and 2 are included in Table VI for comparison.)

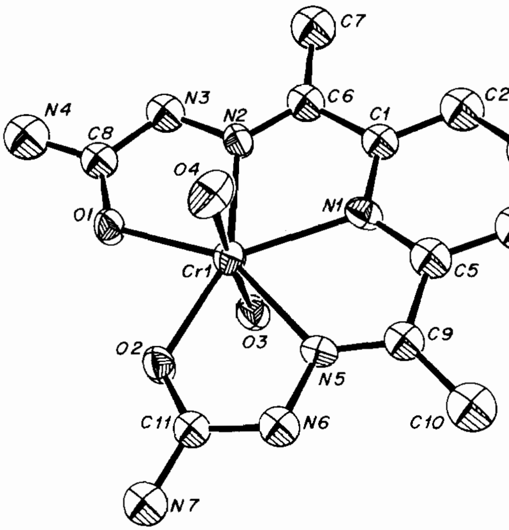


Fig. 1. the structure of $[Cr(DAPSC)(H_2O)_2]^{3+}$ and the numbering scheme of Molecule 1.

The crystal of **II** consists of the pentagonal-bipyramidal $[Cr(DAPSC)(H_2O)_2]^{3+}$ cations, hydrogen bonded to NO_3^- anions and water molecules. The deviations from planarity within each of the semicarbazone arms are small. In Molecule 1 they vary between +0.031 and −0.023 Å in the plane defined by O(1), C(8), N(3), N(2), C(6), C(1) and N(1) and between 0.038 and −0.039 Å in the plane defined by O(2), C(11), N(6), N(5), C(9), C(5) and N(1).

TABLE II. Positional Parameters and Estimated Standard Deviations[a] for II

Atom	x	y	z	Atom	x	y	z
Cr(1)	0.69349(4)	0.01894(9)	0.6769(2)	Cr(2)	0.43892(4)	0.25337(9)	0.8844(2)
O(1)	0.6576(1)	−0.0360(4)	0.8148(7)	O(12)	0.4409(2)	0.1216(4)	0.8544(8)
O(2)	0.7031(2)	−0.1165(4)	0.6602(8)	O(22)	0.3984(2)	0.2099(4)	1.0088(7)
O(3)	0.6610(2)	0.0113(4)	0.4731(7)	O(32)	0.4081(1)	0.2657(4)	0.6779(6)
O(4)	0.7267(2)	0.0338(5)	0.8766(7)	O(42)	0.4711(2)	0.2502(4)	1.0879(7)
N(5)	0.7416(2)	−0.0026(4)	0.5419(8)	N(52)	0.4122(2)	0.3733(4)	0.9856(8)
N(1)	0.7138(2)	0.1460(4)	0.5841(8)	N(12)	0.4638(2)	0.3843(4)	0.8221(8)
N(2)	0.6630(2)	0.1283(4)	0.7523(9)	N(22)	0.4837(2)	0.2305(4)	0.7508(8)
C(11)	0.7290(2)	−0.1476(6)	0.592(1)	C(112)	0.3791(2)	0.2632(6)	1.082(1)
N(7)	0.7348(2)	−0.2348(5)	0.5786(9)	N(72)	0.3545(2)	0.2344(5)	1.1701(9)
N(6)	0.7521(2)	−0.0901(5)	0.5296(9)	N(62)	0.3841(2)	0.3531(4)	1.0686(8)
C(9)	0.7583(2)	0.0608(6)	0.474(1)	C(92)	0.4207(2)	0.4547(5)	0.963(1)
C(10)	0.7885(3)	0.0490(7)	0.373(1)	C(102)	0.4016(3)	0.5362(6)	1.021(1)
C(5)	0.7426(2)	0.1485(6)	0.499(1)	C(52)	0.4519(2)	0.4632(5)	0.870(1)
C(4)	0.7564(3)	0.2290(7)	0.444(1)	C(42)	0.4679(2)	0.5447(6)	0.837(1)
C(3)	0.7380(3)	0.3080(7)	0.477(1)	C(32)	0.4976(2)	0.5418(6)	0.750(1)
C(2)	0.7079(3)	0.3064(7)	0.562(1)	C(22)	0.5110(2)	0.4592(6)	0.700(1)
C(1)	0.6968(2)	0.2229(6)	0.615(1)	C(12)	0.4927(2)	0.3826(5)	0.737(1)
C(6)	0.6669(2)	0.2104(6)	0.709(1)	C(62)	0.5033(2)	0.2911(6)	0.692(1)
C(7)	0.6437(3)	0.2880(7)	0.753(1)	C(72)	0.5323(3)	0.2735(6)	0.589(1)
N(3)	0.6361(2)	0.1041(5)	0.8423(9)	N(32)	0.4902(2)	0.1416(5)	0.7251(9)
N(4)	0.6121(2)	−0.0154(6)	0.968(1)	N(42)	0.4710(2)	−0.0011(6)	0.779(1)
C(8)	0.6360(2)	0.0149(6)	0.875(1)	C(82)	0.4664(2)	0.0876(6)	0.789(1)
N(13)	0.3156(2)	0.4425(5)	0.3113(9)	N(16)	0.9080(2)	0.0320(5)	0.9938(9)
O(43)	0.3082(2)	0.3629(4)	0.280(1)	O(52)	0.9109(2)	−0.0489(4)	0.9741(9)
O(44)	0.3412(2)	0.4765(5)	0.254(1)	O(53)	0.8911(2)	0.0631(5)	1.1032(8)
O(45)	0.2959(2)	0.4872(5)	0.391(1)	O(54)	0.9230(2)	0.0844(5)	0.9051(9)
N(14)	0.5552(3)	0.9782(7)	0.613(1)	N(17)	0.3309(2)	0.1836(6)	0.724(1)
O(46)	0.5810(2)	0.9411(5)	0.569(1)	O(55)	0.3066(2)	0.1344(5)	0.759(1)
O(47)	0.5303(2)	0.9329(5)	0.651(1)	O(56)	0.3314(2)	0.2640(5)	0.756(1)
O(48)	0.5527(2)	1.0629(5)	0.615(1)	O(57)	0.3562(2)	0.1502(4)	0.6510(9)
N(15)	0.8168(3)	0.7681(7)	1.352(1)	N(18)	0.0601(2)	0.2984(6)	0.530(1)
O(49)	0.8339(2)	0.7122(6)	1.287(1)	O(58)	0.0819(4)	0.360(1)	0.554(2)
O(50)	0.7942(3)	0.739(1)	1.426(2)	O(59)	0.0339(4)	0.3130(9)	0.630(2)
O(51)	0.8202(5)	0.8463(7)	1.349(2)	O(60)	0.0585(4)	0.2310(9)	0.459(2)
OL(1)	0.4482(2)	0.2463(5)	0.3651(9)	O(61)	0.0879(5)	0.270(1)	0.452(2)
OL(2)	0.7038(2)	0.0433(5)	0.1546(9)	O(62)	0.0392(5)	0.241(1)	0.560(2)
OL(3)	0.1055(2)	0.1990(6)	0.839(1)	O(63)	0.0583(6)	0.379(1)	0.509(3)
OL(4)	0.6079(2)	0.1188(5)	0.428(1)				

[a] Estimated standard deviations in the least significant digits are shown in parentheses.

The dihedral angle between the two planes is 4.77°.

[UO_2(DAPSC-2H)(H_2O)]·2DMSO (III)

The atomic positional parameters are listed in Table IV. Table V presents important bond lengths and angles. Figure 2 shows the structure and numbering scheme in the complex.

With four molecules in the unit cell of space group $P2_1/n$ there is no crystallographic symmetry imposed upon the complex. The hexagonal-bipyramidal unit, [UO_2(DAPSC-2H)(H_2O)], nearly possesses C_{2v} symmetry. The 2+ charge of the UO_2^{2+} unit is balanced by the doubly deprotonated $(DAPSC\text{-}2H)^{2-}$ ligand and therefore the complex is neutral.

The coordination number of the uranium atom is eight and the sixth position in the hexagonal plane is occupied by a water ligand, weakly bonded to the metal atom (U–O distance of 2.68(1) Å. Each side of the two semi-carbazone side arms deviates only slightly from planarity. The deviations from the plane defined by N(1), C(1), C(6), N(2), N(3), C(8) and O(1) range from 0.030 to –0.097 Å and in the plane defined by O(2), C(11), N(6), N(5), C(9), C(5) and N(1) the deviations are between 0.044 and –0.068 Å. The dihedral angle between the two planes is 11.8°.

TABLE III. Important Bond Lengths (A) and Angles (°) for Molecule **I** in **II**

Lengths (A)			
Cr(1)–O(1)	2.036(5)	N(2)–C(6)	1.29(1)
Cr(1)–O(2)	2.063(5)	N(2)–N(3)	1.37(1)
Cr(1)–O(3)	1.979(5)	C(11)–N(7)	1.33(1)
Cr(1)–O(4)	1.974(5)	C(11)–N(6)	1.37(1)
Cr(1)–N(5)	2.262(7)	C(9)–C(10)	1.50(1)
Cr(1)–N(1)	2.214(6)	C(9)–C(5)	1.46(1)
Cr(1)–N(2)	2.134(6)	C(5)–C(4)	1.41(1)
O(1)–C(8)	1.26(1)	C(4)–C(3)	1.41(1)
O(2)–C(11)	1.27(1)	C(3)–C(2)	1.40(1)
N(5)–N(6)	1.374(9)	C(2)–C(1)	1.40(1)
N(5)–C(9)	1.30(1)	C(1)–C(6)	1.46(1)
N(1)–C(5)	1.36(1)	C(6)–C(7)	1.52(1)
N(1)–C(1)	1.35(1)	N(3)–C(8)	1.36(1)
		N(4)–C(8)	1.33(1)
Angles (°)			
O(1)–Cr(1)–O(2)	77.0(2)	Cr(1)–N(2)–C(6)	124.5(6)
O(1)–Cr(1)–O(3)	93.1(2)	Cr(1)–N(2)–N(3)	114.5(5)
O(1)–Cr(1)–O(4)	89.2(2)	C(6)–N(2)–N(3)	120.8(7)
O(1)–Cr(1)–N(5)	147.2(2)	O(2)–C(11)–N(7)	122.6(7)
O(1)–Cr(1)–N(1)	144.6(2)	O(2)–C(11)–N(6)	119.7(7)
O(1)–Cr(1)–N(2)	74.3(2)	N(7)–C(11)–N(6)	117.6(7)
O(2)–Cr(1)–O(3)	89.2(2)	N(5)–N(6)–C(11)	111.4(6)
O(2)–Cr(1)–O(4)	93.7(3)	N(5)–C(9)–C(10)	126.3(8)
O(2)–Cr(1)–N(5)	70.7(2)	N(5)–C(9)–C(5)	111.5(7)
O(2)–Cr(1)–N(1)	138.3(2)	C(10)–C(9)–C(5)	122.2(8)
O(2)–Cr(1)–N(2)	151.2(2)	N(1)–C(5)–C(9)	114.2(7)
O(3)–Cr(1)–O(4)	176.6(3)	N(1)–C(5)–C(4)	122.5(8)
O(3)–Cr(1)–N(5)	92.2(2)	C(9)–C(5)–C(4)	123.3(8)
O(3)–Cr(1)–N(1)	88.0(3)	C(5)–C(4)–C(3)	116.3(8)
O(3)–Cr(1)–N(2)	88.9(3)	C(4)–C(3)–C(2)	121.9(9)
O(4)–Cr(1)–N(5)	87.0(3)	C(3)–C(2)–C(1)	117.3(9)
O(4)–Cr(1)–N(1)	88.7(3)	N(1)–C(1)–C(2)	122.1(8)
O(4)–Cr(1)–N(2)	89.4(3)	N(1)–C(1)–C(6)	113.9(7)
N(5)–Cr(1)–N(1)	67.9(2)	C(2)–C(1)–C(6)	124.0(8)
N(5)–Cr(1)–N(2)	138.1(3)	N(2)–C(6)–C(1)	112.8(7)
N(1)–Cr(1)–N(2)	70.3(2)	N(2)–C(6)–C(7)	125.0(8)
Cr(1)–O(1)–C(8)	118.7(5)	C(1)–C(6)–C(7)	122.2(8)
Cr(1)–O(2)–C(11)	122.6(5)	N(2)–N(3)–C(8)	112.5(7)
Cr(1)–N(5)–N(6)	115.4(5)	O(1)–C(8)–N(3)	119.8(7)
Cr(1)–N(5)–C(9)	124.4(6)	O(1)–C(8)–N(4)	122.5(8)
N(6)–N(5)–C(9)	120.1(7)	N(3)–C(8)–N(4)	117.6(8)
Cr(1)–N(1)–C(5)	122.0(5)		
Cr(1)–N(1)–C(1)	118.2(5)		
C(5)–N(1)–C(1)	119.8(7)		

TABLE IV. Positional Parameters and Estimated Standard Deviations[a] for **III**

Atom	*x*	*y*	*z*
U	0.46705(2)	0.73271(3)	0.24727(6)
O(1)	0.3646(6)	0.8154(7)	0.301(1)
O(2)	0.5612(7)	0.8126(8)	0.157(2)
O(3)	0.5118(7)	0.7480(6)	0.433(1)
O(4)	0.4213(6)	0.7106(7)	0.062(1)
N(1)	0.4728(5)	0.5640(7)	0.276(1)
N(2)	0.3665(6)	0.6569(7)	0.379(1)
N(3)	0.3100(6)	0.7081(7)	0.432(1)
N(4)	0.2650(9)	0.8460(9)	0.410(2)
N(5)	0.5785(5)	0.6495(7)	0.155(1)
N(6)	0.6330(6)	0.6978(9)	0.097(1)
N(7)	0.6665(8)	0.8378(9)	0.055(2)
Ow	0.4600(8)	0.906(1)	0.190(2)
C(1)	0.4231(6)	0.5187(9)	0.347(1)
C(2)	0.4187(8)	0.4284(9)	0.347(2)
C(3)	0.4667(8)	0.380(1)	0.278(2)
C(4)	0.5234(7)	0.4238(9)	0.213(2)
C(5)	0.5255(7)	0.5150(8)	0.215(1)
C(6)	0.3670(7)	0.5732(8)	0.417(1)
C(7)	0.3129(8)	0.533(1)	0.514(2)
C(8)	0.3153(8)	0.7881(8)	0.374(2)
C(9)	0.5827(6)	0.5641(9)	0.144(1)
C(10)	0.6406(9)	0.519(1)	0.072(2)
C(11)	0.620(1)	0.7820(9)	0.109(2)
S(1)	0.6482(5)	1.0782(5)	0.209(1)
O(5)	0.620(1)	1.023(1)	0.065(2)
C(12)	0.695(1)	1.168(2)	0.159(4)
C(13)	0.563(2)	1.138(2)	0.238(3)
S(2)	0.6723(6)	0.9108(5)	0.613(2)
O(6)	0.7296(9)	0.9708(9)	0.666(2)
C(14)	0.620(1)	0.944(2)	0.521(5)
C(15)	0.699(1)	0.820(2)	0.545(4)

[a] Estimated standard deviations in the least significant digits are shown in parentheses.

TABLE V. Important Bond Lengths (A) and Angles (°) for **III**

Lengths (A)			
U–O(1)	2.34(1)	N(3)–C(8)	1.33(1)
U–O(2)	2.32(1)	N(4)–C(8)	1.33(2)
U–O(3)	1.74(1)	N(5)–N(6)	1.38(1)
U–O(4)	1.76(1)	N(5)–C(9)	1.31(1)
U–N(1)	2.58(1)	N(6)–C(11)	1.31(1)
U–N(2)	2.56(1)	N(7)–C(11)	1.33(2)
U–N(5)	2.60(1)	C(1)–C(2)	1.38(1)
U–Ow	2.68(1)	C(1)–C(6)	1.51(1)
O(1)–C(8)	1.24(2)	C(2)–C(3)	1.34(2)
O(2)–C(11)	1.28(2)	C(3)–C(4)	1.41(2)
N(1)–C(1)	1.35(1)	C(4)–C(5)	1.39(1)
N(1)–C(5)	1.38(1)	C(5)–C(9)	1.48(1)
N(2)–N(3)	1.41(1)	C(6)–C(7)	1.51(1)
N(2)–C(6)	1.32(1)	C(9)–C(10)	1.46(2)

(continued)

Preparation

The results presented here suggest that the formation of the various species is pH dependent and that the extent of deprotonation of the coordinated DAPSC ligand is also related to the nature of the metal center in the complex. Compounds **I** and **Ia** are obtained when the pH of the solution is about 3, indicating that the coordinated DAPSC is fairly acidic. Aqueous solutions of **I** and **Ia** are slightly acidic due to the hydrolysis of H_2O ligands in the

TABLE V. *(continued)*

Angles (°)			
O(1)–U–O(2)	115.1(4)	N(1)–U–Ow	174.8(4)
O(1)–U–O(3)	91.0(5)	N(2)–U–N(5)	123.3(3)
O(1)–U–O(4)	90.3(5)	N(2)–U–Ow	120.6(4)
O(1)–U–N(1)	122.5(3)	N(5)–U–Ow	116.0(4)
O(1)–U–N(2)	61.4(3)	U–O(1)–C(8)	124.6(9)
O(1)–U–N(5)	173.1(4)	U–O(2)–C(11)	127.0(1)
O(1)–U–Ow	59.4(4)	U–N(1)–C(1)	122.3(8)
O(2)–U–O(3)	89.2(5)	U–N(1)–C(5)	121.3(7)
O(2)–U–O(4)	93.1(5)	C(1)–N(1)–C(5)	116(1)
O(2)–U–N(1)	122.3(3)	U–N(2)–N(3)	119.4(7)
O(2)–U–N(2)	172.4(4)	U–N(2)–C(6)	124.8(8)
O(2)–U–N(5)	60.8(4)	N(3)–N(2)–C(6)	115.4(1)
O(2)–U–Ow	55.8(4)	N(2)–N(3)–C(8)	107(1)
O(3)–U–O(4)	176.6(5)	U–N(5)–N(6)	118.6(8)
O(3)–U–N(1)	91.8(4)	U–N(5)–C(9)	124.3(7)
O(3)–U–N(2)	84.2(5)	N(6)–N(5)–C(9)	116.6(1)
O(3)–U–N(5)	94.5(4)	N(5)–N(6)–C(11)	110(1)
O(3)–U–Ow	93.0(5)	N(1)–C(1)–C(2)	124(1)
O(4)–U–N(1)	84.8(4)	N(1)–C(1)–C(6)	116(1)
O(4)–U–N(2)	93.7(4)	C(2)–C(1)–C(6)	120(1)
O(4)–U–N(5)	84.4(4)	C(1)–C(2)–C(3)	120(1)
O(4)–U–Ow	90.4(5)	C(2)–C(3)–C(4)	119(1)
N(1)–U–N(2)	61.8(3)	C(3)–C(4)–C(5)	119(1)
N(1)–U–N(5)	61.6(3)	N(1)–C(5)–C(4)	122(1)
N(1)–C(5)–C(9)	117(1)	N(3)–C(8)–N(4)	115(1)
C(4)–C(5)–C(9)	121(1)	N(5)–C(9)–C(5)	115(1)
N(2)–C(6)–C(1)	114(1)	N(5)–C(9)–C(10)	123(1)
N(2)–C(6)–C(7)	123(1)	C(5)–C(9)–C(10)	122(1)
C(1)–C(6)–C(7)	122(1)	O(2)–C(11)–N(6)	123(1)
O(1)–C(8)–N(3)	127(1)	O(2)–C(11)–N(7)	119(1)
O(1)–C(8)–N(4)	118(1)	N(6)–C(11)–N(7)	118(1)

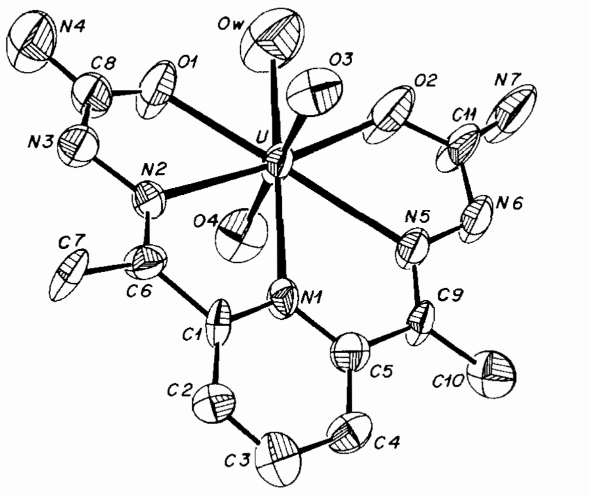


Fig. 2. The structure and the numbering scheme of [UO_2-(DAPSC-2H)(H_2O)].

complex and deprotonation of the second NH group. Compound **II** was obtained by lowering the pH of the solution and shifting the equilibrium towards the protonated species.

The UO_2^{2+} unit is known to cause deprotonation of coordination ligands with R–N=N(H)–R systems [8]. Furthermore, the acetate ions of the starting material serve as base and promote deprotonation of DAPSC. Compound **III** was obtained from undried DMSO in the open and this is probably the source of the H_2O ligand in the complex.

Comparison and Correlation of Structure

Our preliminary experiments in which aqueous solutions of **I** were found to be acidic rather than basic (as expected from its previous formulation [4]), were follwed by a detailed X-ray study of **I** in our laboratory. The results confirmed the structure reported in the previous study except for one crucial detail. No electron density, corresponding to a hydrogen atom, was located near N(3), the semi-carbazone NH nitrogen, as reported by Palenik *et al.* [4]. The presence of this atom, H(1), in the reported position is highly improbable because N(3), the 'NH' nitrogen serves as an acceptor in a hydrogen bond with a water ligand of a neighboring complex, O(4). The calculated distance between the two hydrogen atoms H(1) and H(19), the H_2O hydrogen, is ~1.5 Å and the H(1)–N(3)··· H(19) angle is ~40°. The short distance and the acute angle, together with the fact that the reported thermal parameter of H(1) is extremely high (B = 12 Å^2) [4], imply that H(1) does not exist in **I** and that the N(3)–H group in this arm of the semi-carbazone ligand underwent deprotonation. As a result, the overall charge of the complex is 2+ rather than 3+. This charge is balanced by the two NO_3^- ions and no OH^- ion is present in the crystal. Deprotonation of an NH group in DAPSC permits the formation of a conjugated system and thereby a delocalization of the negative charge as in 2. Such a phenomenon in related ligands is not unusual and this process is enhanced by the high effective positive charge of metal ions such as Cr(III), In(III), Sc(III) and U(VI) and by the stabilization energy gained by the delocalization [8, 9]. The formation of a conjugated system in the deprotonated ligand may explain the deep colors of the d^0 complex of [Sc(III)(DAPSC-H)-$(H_2O)_2]^{2+}$ [6] and of [In(III)(DAPSC-H)$(H_2O)_2]^{2+}$ [7]. A detailed spectroscopic study of the UO_2^{2+} complex will be published elsewhere.

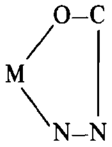
Another interesting feature of **I**, **Ia** and the In(III) and Sc(III) complexes, in which only one arm of the ligand is deprotonated, is the distortion from C_2 symmetry which in the case of Cr(III) is very pronounced, as can be seen from Table VI. This distortion is the result of the stronger attraction of the negatively charged section of the semi-carbazone arms to the positive metal ion. This interaction decreases the M–O(1) and M–N(2) distances and

TABLE VI. Structural Data for M(DAPSC), M(DAPSC-H) and M(DAPSC-2H)

Complex	Bond distances (A)				Reference
	M–O(1)	M–O(2)	M–N(2)	M–N(5)	
$[Cr(DAPSC\text{-}H)(H_2O)_2]^{2+}$ (**I**)	1.979(3)	2.173(3)	2.023(3)	2.397(4)	4
$[Cr(DAPSC\text{-}H)(H_2O)_2]^{2+}$ (**Ia**)	1.965(3)	2.117(3)	2.051(4)	2.399(4)	this work
$[Sc(DAPSC\text{-}H(H_2O)_2]^{2+}$	2.098(3)	2.137(3)	2.258(4)	2.305(4)	6
$[In(DAPSC\text{-}H)(H_2O)_2]^{2+}$	2.151(5)	2.216(5)	2.257(5)	2.310(5)	7
$[Cr(DAPSC)(H_2O)_2]^{3+}$ (**II**)	2.036(5)	2.063(5)	2.134(6)	2.262(7)	
	1.986(5)	2.045(6)	2.150(6)	2.262(6)	this work
$[Fe(DAPSC)Cl_2]^+$	2.131(4)	2.074(4)	2.200(5)	2.203(6)	4
$[UO_2(DAPSC\text{-}2H)(H_2O)]$ (**III**)	2.34(1)	2.32(1)	2.56(1)	2.60(1)	this work

the resulting stress on the ligand causes an increase in the M–O(2) and M–N(5) distances in the opposite side of the system. In the case of Cr(III) in **I** and **Ia** this effect is enhanced by the existence of the Jahn–Teller effect in the d^3 system under the pentagonal bipyramidal field [10]. It is interesting to compare the extent of the distortion in the deprotonated ligand as in **I** or **Ia** and in the protonated ligand as in **II**. From Table VI it can be seen that the net contribution of the Jahn–Teller effect to the distortion of the geometry as expressed by the difference between the M–N(2) and M–N(5) distances, is relatively small. This difference is about 0.12 Å in **II** whereas the addition of the charge effect in **I** and **Ia** brings about a remarkable difference of about 0.35 Å. The greater distortions in the Cr(III) complexes **I** and **Ia**, compared with those found in the Sc(III) and In(III) complexes (differences of about 0.05 Å in M–N(2) and M–N(5) bonds [6, 7]) is probably the result of the greater effective charge of the Cr^{3+} ion and the existence of the Jahn–Teller effect.

As mentioned earlier, deprotonation of an NH group of one of the semi-carbazone arms permits the existence of several resonance configurations. Such resonance should affect the bond distances in this arm. From the bond distances it is clear that such an effect does exist although it is not a simple one because ligand–metal bonding introduces other factors. The delocalization of the π electrons in the deprotonated arm, as in **2** or **3**, should lengthen the C=O, and the N=C double bonds and shorten the C–N and N–N single bonds. In general, this is demonstrated in all structures in which single or double deprotonation occurs. The only exception is the N–N single bond length which increases rather than decreases. This is probably the result of the stress in the five membered ring due to the strong attraction of the negatively charged unit to the metal atom.



Supplementary Material

Tables of structure factors, thermal parameters, non-essential bond distances and angles for **II** and **III** and all crystallographic material for **Ia** (69 pages) are available from the authors.

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