Inorganica Chimica Acta, 10 (1974) 41–45

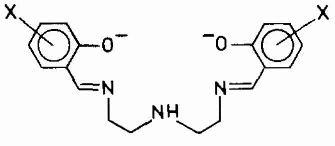
Seven-Co-Ordinate Uranyl Compounds with Planar Quinquedentate [N_3O_2] Salicylaldiminato Ligands

E. D. McKENZIE, R. E. PAINE and S. J. SELVEY
Chemistry Department, The University, Sheffield S3 7HF U.K.
Received November 28, 1973

The dianion of the ligand N,N'-bissalicylidene-1,5-diimino-3-azapentane acts as a planar quinque-dentate to metal species with a large covalent radius such as uranyl. The dioxouranium(VI) compounds of this and related ligands (with 5-Cl, 5-Br, 3-OMe, 3,5-diCl or 5,6-benzo substituents on the salicyl moiety) are examples of 2 + 5 co-ordination at the metal. A number of solvates were obtained and characterised by their X-ray diffraction patterns and i.r. spectra. One of these undergoes heterogeneous exchange reactions with consequent changes in the dimensions of the crystalline lattice. By contrast, the longer ligand systems based on the triamines 1,7-diamino-4-aza-heptane and 1,7-diamino-4-aza-4-methyl-heptane are much more reluctant to form seven-co-ordinate uranium(VI) compounds. These ligands, with trimethylenediamine chelate rings appear to be too large for ideal co-ordination to the metal.

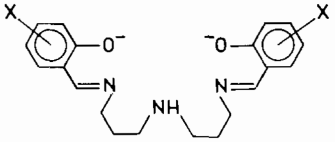
Introduction

We are investigating the structures of metal compounds with ligands of unconventional geometry which do not fit (except with gross distortion) any of the regular co-ordination polyhedra. The potentially quinquedentate ligand I* belongs to this class in its compounds with the first-row transition metals, being unable to use all five of its donor atoms at the same metal. Details of some compounds of these metals will be reported elsewhere.



I

However molecular models indicated that I could act as a planar quinquedentate ligand when the metal to donor atom distance was greater than ~ 2.3 Å. Accordingly, we made a uranyl compound to demonstrate this mode of bonding.[1] The range of compounds obtainable has now been explored further using some substituted salicylaldehydes as well as the longer triamines of the ligands II. We were also interested in looking for further examples of the interesting crystalline solvates, which had been observed[1] for [UO_2(diensal)].



II

The general problem of the variety of uranyl compounds obtainable with chelating ligands has been receiving some attention recently.[2,3]

Experimental

Preparation of Compounds

The various compounds of the ligands I were made by adding stoicheiometric amounts of uranyl acetate in ethanol (~ 2.0 g/50 ml) to the ligand in ethanol (~ 1.5 g/50 ml).[4] The solutions of the latter were prepared directly from the aldehyde and diethylentriamine (1,5-diamino-3-azapentane) in 2:1 molar ratio. The products were filtered off, washed with solvent, and dried in the air.

[UO_2(diensal)] separated out as the ethanol solvate, which slowly lost ethanol in the air; but recrystallised as the solvate when suspended in the solvent.

Recrystallisation from Me_2SO gave a 1:1 solvate. From MeCN either orange needles of [UO_2(diensal)] MeCN, or yellow prisms of [UO_2(diensal)] – often mixtures of both – was obtained; but when the MeCN solvate was left in contact with the solvent at room temperature or at the boiling point it redissolved and was replaced by crystals of the latter.

---

* I is abbreviated as *diensal* for X = H and as *dien-X-sal* for the various species substituted on the salicyl moieties. II, similarly, is abbreviated as *dptsal*.

TABLE I. The Compounds Prepared, their Colours and the Analytical Data.

Compound	Colour	Analyses							
		Found				Calculated			
		C	H	N	Other	C	H	N	Other
$[UO_2(diensal)]$	yellow	37.5	3.4	7.0		37.3	3.3	7.3	
$[UO_2(diensal)]EtOH$	orange	38.2	4.1	6.8		38.4	4.0	6.7	
$[UO_2(diensal)]MeCN$	orange	38.9	3.8	8.9		38.7	3.6	9.0	
$[UO_2(diensal)]Me_2SO$	orange	36.8	3.9	6.3	S, 5.1	36.5	3.8	6.4	S, 4.9
$[UO_2(diensal)]CHCl_3$	yellow	33.2	3.3	5.9	Cl, 15.2	32.7	2.9	6.0	Cl, 15.2
$[UO_2(diensal)]C_6H_6$	red	44.5	4.1	6.0		43.8	3.8	6.4	
$[UO_2(dien\text{-}3\text{-}OMe\text{-}sal)]$	red-orange	37.4	3.9	6.5		37.6	3.6	6.6	
$[UO_2(dien\text{-}3\text{-}OMe\text{-}sal)]H_2O$	red-orange	37.3	3.9	6.5		36.5	3.8	6.4	
$[UO_2(dien\text{-}3\text{-}OMe\text{-}sal)]0.5MeCN$	red	37.9	4.0	7.0		38.2	3.6	7.4	
$[UO_2(dien\text{-}3\text{-}OMe\text{-}sal)]Me_2SO$	red–orange	37.2	3.9	6.2	S, 4.6	36.8	4.1	5.9	S, 4.5
$[UO_2(dien\text{-}3\text{-}OMe\text{-}sal)]C_6H_6$	orange	43.1	4.1	6.1		44.5	4.3	6.2	
$[UO_2(dien\text{-}5\text{-}Cl\text{-}sal)]$	orange–yellow	33.3	2.9	6.7	Cl, 11.0	33.4	2.6	6.5	Cl, 11.0
$[UO_2(dien\text{-}5\text{-}Br\text{-}sal)]$	orange	29.3	2.5	5.6		29.3	2.3	5.7	
$[UO_2(dien\text{-}3,5\text{-}diCl\text{-}sal)]$	yellow	30.2	2.5	6.1	Cl, 19.8	30.3	2.1	5.8	Cl, 19.8
$[UO_2(dien\text{-}3,5\text{-}diCl\text{-}sal)]MeCN$	orange	31.6	2.9	6.5	Cl, 16.9	31.7	2.4	7.4	Cl, 18.7
$[UO_2(dien\text{-}3,5\text{-}diCl\text{-}sal)]Me_2SO$.	red–orange	30.8	3.1	5.1	Cl, 17.7; S, 4.0	30.2	2.7	5.3	Cl, 17.8; S, 4.0
$[UO_2(dien\text{-}5,6\text{-}benzo\text{-}sal)]$	orange	46.3	3.8	6.4		46.0	3.4	6.2	
$[UO_2(dptsal)]EtOH$	red–orange	39.9	4.4	6.4		40.1	4.2	6.5	
$[UO_2(dptsal)]MeCN$	orange	40.6	4.2	8.4		40.6	4.3	8.6	
$[UO_2(dpt\text{-}5\text{-}Cl\text{-}sal)]$	orange	35.9	3.1	6.4	Cl, 10.2	35.5	3.1	6.2	Cl, 10.5
$[UO_2(dpt\text{-}5\text{-}Cl\text{-}sal)]$	orange	37.2	3.4	7.8	Cl, 9.9	36.8	3.4	7.8	Cl, 9.9
$[UO_2(dpt\text{-}5,6\text{-}benzo\text{-}sal)]$	red–orange	48.4	4.3	6.1		47.5	3.7	5.9	

TABLE II. Some of the Characteristic I.R. Stretching Frequencies, and the X-ray Powder Diffraction Data.

Compound	Stretching frequencies		Observed X-ray Diffraction Lines (2Θ in degrees)^a
	NH	Solvent of crystallisation	
$[UO_2(diensal)]$	3242s		9.39s, 13.71w, 16.15vw, 18.73s, 21.83m, 25.05w, 25.77w, 27.40m, 32.85m
$[UO_2(diensal)]EtOH$	3200m^b	3400m, br(OH)	10.02s, 11.33w, 13.87m, 14.88m, 17.58m, 18.06m, 21.01ms, 23.60ms, 25.58m, 33.64m, 35.20w
$[UO_2(diensal)]MeCN$	3200m^b	2250w(C≡N)	10.13s, 10.63ms, 14.11m, 14.71ms, 17.41m, 18.41m, 21.22ms, br, 23.07m, 23.73ms, 25.62m, 26.17w, 32.69m, 35.32m
$[UO_2(diensal)]Me_2SO$	3255w, sp, sh 3195s^b	1040ms, br(S=O)	9.82s, 10.02vw, 13.86ms, 14.24w, 14.56m, 17.03m, 19.14w, 21.57ms, 22.32w, 23.82m, 24.47w, 24.89w, 31.69m, 33.52m
$[UO_2(diensal)]CHCl_3$	3195s^b		10.26s, 12.16m, 14.06s, 19.23s, 20.69w, 20.88w, 21.89ms, 22.77s, 24.70m, 25.67m, 27.71m, 31.52m, 33.65m, 35.90m
$[UO_2(diensal)]C_6H_6$	3217s^b	3030w(CH)	10.41s, 12.41m, 13.60ms, 18.42m, br, 19.68m, 20.80m, 22.23m, 35.28m, 36.90m, 41.98m

TABLE II. (Cont.)

Compound	Stretching frequencies		Observed X-ray Diffraction Lines (2 Θ in degrees)[a]
	NH	Solvent of crystallisation	
[UO$_2$(dien-3-OMe-sal)]	3193s[c]		9.78s, 10.33w, 14.09m, 14.89m, 17.32m, 19.29m, 21.74ms, 22.89m, 24.06ms, 26.94w, 32.40ms, 34.01m, 35.75m, 40.15m
[UO$_2$(dien-3-OMe-sal)]H$_2$O	3285m 3240s, br 3210ms, sh	3460s, br(OH)	6.18s, 9.63ms, 12.38, 15.08m, 16.38s, 17.13m, 20.23m, 24.08m, 25.48m, 26.38ms, 29.08m, 30.63m, 31.58ms, 33.18m
[UO$_2$(dien-3-OMe-sal)]0.5MeCN	3205s[d]	2243m, sp(C≡N)	10.23s, 10.63s, 13.96m, 17.55m, 18.57m, 21.18ms, 31.74m, 32.61m, 34.20m
[UO$_2$(dien-3-OMe-sal)]Me$_2$SO	3255w, sp 3170s	1010m(S=O)	9.53w, 10.01s, 12.32w, 13.23m, 15.36w, 15.77m, 19.55m, 20.83w, 27.80m, 30.11m
[UO$_2$(dien-3-OMe-sal)]C$_6$H$_6$	3255m, sh 3240m, sh 3218s 3200s, sh	3030w(CH)	9.53ms, 10.58s, 11.76w, 12.86w, 15.56m, 17.34s, 19.28ms, 22.71m, 23.22m, 26.48m, 34.2ms, 34.8m
[UO$_2$(dien-5-Cl-sal)]	3250s		8.34s, 13.27w, 16.18ms, 16.70m, 18.22s, 20.58w, 21.99ms, 23.46w, 25.33m, 30.14m, 32.61w, 37.62m, 45.92w
[UO$_2$(dien-5-Br-sal)]	3245s		8.50ms, 16.60s, 18.54ms, 22.24m, 23.51w, 25.98w, 27.11mw, 29.94m, 32.49m, 33.30m
[UO$_2$(dien-3,5-diCl-sal)]	3262m, sp, sh 3258m, sp, sh 3250m, sp, sh 3240s, sp		7.74m, 8.85ms, 12.58w, 13.54m, 15.5m, 16.0m, 17.34s, 19.00m, 21.26m, 23.24m, br, 27.96m, 29.12m, 30.41m, 31.54m, 32.78m
[UO$_2$(dien-3,5-diCl-sal)]MeCN	3203s[e]	2282m, sp(C≡N)[f] 2245s, sp(C≡N)	11.2m, 12.4m, 13.7ms, 16.3w, 20.0m, 20.9m, 25.2m, 30.7m
[UO$_2$(dien-3,5-diCl-sal)]Me$_2$SO	3147s	1050m(S=O)	10.20m, 10.78m, 14.7w, 16.69s, 18.81m, 19.94m, 20.83w, 22.26w, 25.43m, 30.14m
[UO$_2$(dien-5,6-benzo-sal)]	3240s		7.35vs, 14.67m, 16.11ms, 17.72ms, 19.34m, 21.31m, 22.01m, 24.95m, 25.40w, 26.48ms, 29.8m, br, 36.13m
[UO$_2$(dptsal)]EtOH	3255s, sp,	3400s, br(OH)	10.25s, br, 13.34m, 14.54m, 17.06w, 17.48m, 20.30s, 22.83m, 24.47w, 33.51m
[UO$_2$(dptsal)]MeCN	3265m, sp 3250ms, sp	2300w, sp(C≡N)[f] 2255ms, sp(C≡N)	10.56s, br, 10.35w, 13.82m, 15.27m, 18.19w, 18.86m, 21.03mw, 22.48ms, 28.31m
[UO$_2$(dpt-5-Cl-sal)]	3255s, sp		9.00s, 12.38w, 15.77vs, 17.88w, 20.23m, 25.19m
[UO$_2$(dpt-5-Cl-sal)]MeCN	3245s, sp	2280w, sp(C≡N)[f] 2250m, sp(C≡N)	12.24w, 14.83ms, 16.29w, 20.86m, 22.16w, 35.54m
[UO$_2$(dpt-5,6-benzo-sal)]	3235s, sp 3210w, sh		9.96s, br, 12.23w, 14.79s, 18.33ms, 19.25ms, 21.28m, 22.48m, 23.54ms, 30.04w, 31.20w, 33.26w, 35.19m

(s = strong, m = medium, w = weak, v = very, sp = sharp, and sh = shoulder).

---

[a] Co–Kα radiation; We list all of the first six observed lines, together with up to eight more of the more characteristic lines to higher angle. [b] These spectra also generally had an absorption at 3240 cm^{-1}, which varied in intensity between different samples. It almost certainly results from contamination with the non-solvated material. [c] Absorption bands were also observed at 3590m, 3545ms, and 3518m. We observe such bands in a variety of compounds. They appear to be combination bands. [d] Also bands at 3570m, 3527s (see c). [e] Also a band at 3555w, sp (see c). [f] These may be overtone or combination bands, not associated with the C≡N group.

The compound was not sufficiently soluble to be recrystallised from CCl_4, $CHCl_3$ or benzene, but changes did occur when $[UO_2(diensal)]EtOH$ {but not $[UO_2(diensal)]$} was suspended in them. In hot CCl_4 (or when heated in water or in the air) yellow $[UO_2(diensal)]$ was obtained; but, by contrast, both $CHCl_3$ and benzene replaced the ethanol in the crystalline compound at room temperature.

$[UO_2(dien\text{-}3\text{-}OMe\text{-}sal)]$. Cold ethanol solutions of the components gave the non-solvate; but, if a uranyl solution was added to a hot ligand solution, a hydrate separated out. Recrystallisation from a variety of solvents, including benzene, gave in each case a crystalline solvate (Tables I and II).

For the other dien ligand compounds, reaction products were nonsolvates, and only the 3,5-dichlorosalicyl compound gave crystalline solvates from Me_2SO and MeCN. The others 'recrystallised' unchanged.

For the dpt ligand compounds (II), pure crystalline samples were obtainable only with some difficulty.

$[UO_2(dptsal)]EtOH$ and $[UO_2(dpt\text{-}5\text{-}Cl\text{-}sal)]$ separate in tolerably pure form from ethanol, provided one uses an excess of ligand (~ 3 times). They can be recrystallised from MeCN, whence they are obtained as 1 : 1 solvates (Table I).

$[UO_2(dpt\text{-}5,6\text{-}benzo\text{-}sal)]$ also is obtainable by this method, but always in grossly impure form. Recrystallisation from MeCN gives a reasonably pure crystalline product.

Neither $[UO_2(dpt\text{-}3\text{-}OMe\text{-}sal)]$ nor $[UO_2(dpt\text{-}3,5\text{-}diCl\text{-}sal)]$ were obtainable from ethanol. The products were invariably amorphous, and, although the analytical data sometimes were close to the expected values, there is no evidence that the 1 : 1 molecular species is obtainable under these conditions.

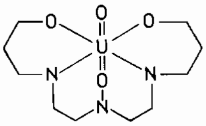
Physical Measurements

The following instruments were used: X-ray diffraction, Phillips 11.46 cm Debye–Scherrer camera with Co-Kα radiation; i.r. spectra, Perkin--Elmer PE457.

Results and Discussion

In all cases the compounds have been defined by their X-ray powder diffraction patterns (Table II), as well as the i.r. spectra and analyses (Tables I and II). The X-ray data show that $[UO_2(dien\text{-}5\text{-}Cl\text{-}sal)]$ and $[UO_2(dien\text{-}5\text{-}Br\text{-}sal)]$ are isomorphous.

The three-dimensional X-ray structural analysis[1,5] of $[UO_2(diensal)]$ has confirmed the original assignment of structure as that of type III, in which the quinquedentate dianion ligand is bound equatorially to the uranyl group. And, it is a reasonable assumption that the rest of the compounds listed in Table I also have this structure (complete proof, of course, would require a full three-dimensional X-ray study of each and every crystalline species since no other physical methods are available for determining detailed structure here). The compounds listed in Table I have solubility properties attributable to monomeric compounds of type III and can be recrystallised readily from various solvents.

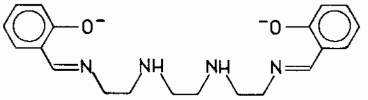


III

The contrast between the number of compounds obtainable with the dien ligands I and those with the larger dpt ligands II is very marked (see the listing in Table I). With the latter, amorphous products often separated from the ethanol reaction mixtures. They were characterised by i.r. spectra with ill-defined broad bands, especially by a broad envelope covering the region 2200–3800 cm^{-1} with broad peaks at ~3000 and 3400 cm^{-1}. These amorphous materials appear to represent mixed polymeric materials of the type $[(UO_2)_x(L)_y(L')_z]_n$ (where L represents the ligands II and L′ some other unidentate ligands like water or ethanol), and were generally insoluble; although some solvents (*e.g.* benzene) did remove part of the organic ligand. They were sometimes but much less often encountered in the dien ligand systems also. Only three of the dpt ligands gave crystalline compounds which appear to be of type III; and, when we attempted to use the N-methyl analogue of II, none of the potentially quinquedentate ligands gave *crystalline* 1 : 1 monomeric products.

It seems that with the ligands II we are on the fringes of stability of the 1 : 1 compounds III. That is, the ligands with trimethylene chelate rings, having a significantly greater 'bite' at the metal, are too large for ideal bonding at the uranyl. The methyl group on the N-Me-dpt ligands probably contributes further to this steric over-crowding, and may explain our failure to obtain any 1 : 1 compounds with this ligand.

Apropos the ideal ligand size for bonding at uranyl, we have been looking at the possibility that the ligand (IV) might give an example of 2 + 6 co-ordination at the uranium; but the material obtained from ethanol has little crystallinity, and cannot be recrystallised. Its behaviour with various solvents (partial 'solution' from which no crystals can be obtained, and always leaving a residue) suggests to us that the orange-yellow product is a mixture of ill-defined polymeric materials.



IV

Solvates

The existence of the crystalline solvates (Table I) is generally unremarkable for such molecular species; but those of [UO$_2$(diensal)] are unusual in several ways.

[UO$_2$(diensal)]MeCN is metastable. It often crystallises first from super-saturated solutions in this solvent, but then slowly redissolves and is replaced by [UO$_2$(diensal)]. In contact with the solvent, the solid in ***equilibrium*** with the solution either at room temperature or at the boiling point of MeCN is always the non-solvate. So the formation of crystals of the solvate is a kinetically determined process. By contrast, it is the isomorphous (Table II) ethanol solvate that is in equilibrium with ethanol solutions, and [UO$_2$(diensal)] can be converted to the solvate merely by suspending it in ethanol at room temperature.

[UO$_2$(diensal)]EtOH undergoes heterogeneous exchange reactions with other solvents. Thus, both benzene and chloroform replace the ethanol at room temperature with change in colour (Table I) and in the X-ray powder patterns (Table II). These changes do not result from 'recrystallisations'. Indeed the compound has very little solubility in either solvent; the dilute benzene solution is pale yellow; and no change occurs when [UO$_2$(diensal)] is suspended in either solvent. So the benzene or chloroform molecules must be replacing the ethanol in the crystalline lattice through channels in the structure (details of which should become clear from an X-ray analysis of the ethanol solvate now being undertaken by Drs. A.J. Smith and M.N. Akhtar). The X-ray powder diffraction patterns of the products are sufficiently like that of the original ethanol solvate (although quite distinctive) to allow us to conclude that major changes in the crystalline structure do not occur – probably just small changes in the unit cell dimensions. The colour changes between these different solvates probably reflect small variations in the overall conformation of the molecule and thus different couplings of the azomethine chromophores.

None of the other compounds investigated showed parallel behaviour. [UO$_2$(dien-3-OMe-sal)] was more soluble, but, although it formed a similar range of solvates, all of them were obtained by normal recrystallisation processes.

There is no good reason for seeing[3] the solvent molecules as co-ordinated to the metal in any of the materials. The quinquedentate ligands would appear to satisfy totally the co-ordination requirements of the metal, and as more X-ray structural data become available,[6] it seems that 5 + 2 co-ordination is the most common for uranyl compounds.

References

1 M.N. Akhtar, E.D. McKenzie, R.E. Paine and A.J. Smith, *Inorg. Nuclear Chem. Letters,* 1969, *5,* 673.

2 L. Cattalini, U. Croatto, S. Degetto and E. Tondello, *Inorg. Chim. Acta Reviews,* 1971, *5,* 19; G. Bor, L. Magon, L. Maresca and G. Natile, *J.C.S. Dalton,* 1973, 1308; and references therein.

3 L. Cattalini, S. Degetto, M. Vidali and P.A. Vigato, *Inorg. Chim. Acta,* 1972, *6,* 173.

4 M. Augustin, H.J. Kerrinnes and W. Langenbeck, *J. prakt. Chem.,* 1964, *26,* 130.

5 M.N. Akhtar and A.J. Smith, *Acta Cryst.,* 1973, B29, 275.

6 G. Bandoli, D.A. Clemente, U. Croatto, M. Vidali and P.A. Vigato, *Chem. Commun.,* 1971, 1330; G. Bandoli, L. Cattalini, D.A. Clemente, M. Vidali and P.A. Vigato, *Chem. Commun.,* 1972, 344; G. Bandoli, D.A. Clemente, F. Benetollo, M. Vidali, P.A. Vigato and U. Castellato, *Inorg. Nuclear Chem. Letters* 1973, *9,* 433; G. Bombieri, S. Degetto, G. Marangoni, R. Graziani and E. Forsellini, *Inorg. Nuclear Chem. Letters,* 1973, *9,* 233; and references therein.