La présence de l'ion ammonium a été mise en évidence qualitativement par la réaction de la solution aqueuse du produit avec le tétraphénylborate de sodium et quantitativement par l'analyse élémentaire. La teneur en azote du composé étudié est de 8,05% selon cette dernière et de 8,14% selon la formule indiquée ci-dessus.

L'ion ammonium a été identifié parmi les molécules d'eau grâce à l'étude des environnements. La maille contient 12 NH_4^+. Les positions occupées par O(13) et O(14) ne peuvent convenir pour l'atome N puisqu'elles introduisent respectivement six et deux atomes par maille. Seule est possible l'une des trois positions N(10), O(11) et O(12). N(10) est entouré de $O(8^{i})$, $O(8^{ii})$, $O(9^{i})$, $O(11^{i})$, $O(12^{ii})$ et $O(13^{iii})$ dont les distances à N(10) appartiennent à l'intervalle 2,78(2)-3,16(2) Å. N(10) paraît réaliser quatre liaisons hydrogène dont deux peuvent être des liaisons bifurquées en raison de la proximité de $O(8^{i})$ et de $O(9^{i})$ d'une part, de $O(8^{ii})$ et de $O(12^{ii})$ d'autre part. O(11) et O(12) ont chacun trois voisins situés à des distances comprises entre 2,74(2) et 3,02(3) Å. Autour de O(11), on trouve $O(8^{iv})$, O′(9) et $N(10^{vi})$ [code de symétrie: (vi) $y, 1 - x + y, \frac{1}{2} + z$] et autour de O(12), O(8), $O'(6^{v})$ et $N(10^{ii})$. La somme des angles formés par les droites joignant O(11) ou O(12) à leurs voisins respectifs est de 359,5° dans le cas de O(11) et de 312,3° dans le cas de O(12). On a donc vraisemblablement sur chacune de ces positions l'atome O d'une molécule d'eau. Ainsi, la position la plus probable pour l'atome N de NH_4^+ est N(10).

O(14) est situé sur un axe ternaire en $z = \frac{1}{4}$. Il en résulte que chacun des atomes d'hydrogène qui lui sont liés peut occuper, en désordre statistique, jusqu'à six positions.

Les listes des facteurs de structure, des coefficients d'agitation thermique anisotrope, des coordonnées des atomes d'hydrogène, des angles de torsion, des distances des atomes de l'anion aux plans moyens et des distances entre atomes appartenant à des entités chimiques différentes ont été déposées aux archives de la British Library Document Supply Centre (Supplementary Publication No. SUP 71396: 16 pp.). On peut en obtenir des copies en s'adressant à: The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, Angleterre. [Référence de CIF: DU1047]

Références

B. A. Frenz & Associates, Inc. (1982). *SDP Structure Determination Package*. College Station, Texas, EU.

Johnson, C. K. (1976). *ORTEP*II. Rapport ORNL-5138. Oak Ridge National Laboratory, Tennessee, EU.

Khodadad, P. & Rodier, N. (1992). *Acta Cryst.* C**48**, 2029–2031.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1982). *MULTAN*11/82. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. de York, Angleterre, et de Louvain, Belgique.

Viossat, B., Khodadad, P. & Rodier, N. (1990). *Acta Cryst.* C**46**, 2062–2065.

Viossat, B., Khodadad, P. & Rodier, N. (1991*a*). *Acta Cryst.* C**47**, 179–180.

Viossat, B., Khodadad, P. & Rodier, N. (1991*b*). *Acta Cryst.* C**47**, 1714–1716.

Viossat, B., Khodadad, P. & Rodier, N. (1993). *Acta Cryst.* C**49**, 1370–1372.

Viossat, B., Khodadad, P., Rodier, N. & Guillard, O. (1990). *Acta Cryst.* C**46**, 894–896.

Viossat, B., Rodier, N., Nguyen-Huy, D. & Guillard, O. (1986). *Acta Cryst.* C**42**, 659–662.

Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 159–166.

Acta Cryst. (1994). C**50**, 48–52

Structures of *catena*-Poly[(nitrato-*O*,*O′*)-silver(I)-*μ*-(di-2-pyridyl ketone-*N*:*N′*)] and Di-2-Pyridyl Ketone

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Abstract

An X-ray structural analysis of *catena*-poly[(nitrato-*O*,*O′*)silver(I)-*μ*-(di-2-pyridyl ketone-*N*:*N′*)] (I) and di-2-pyridyl ketone (II) [2-(2-pyridinecarbonyl)pyridinium tetrafluoroborate] revealed the first two examples of di-2-pyridyl ketone (DPK) where hydration of the carbonyl function has not occurred. In compound (I), the crystals were found to consist of $Ag(DPK)^+$ repeating units, in which Ag^+ attains a distorted tetrahedral coordination environment. By coordinating through the two pyridyl N atoms, DPK is observed to bridge separate Ag^+ cations resulting in a non-cross-linked metal containing an extended structure. Single crystals of compound (II) were found to contain monoprotonated DPK molecules balanced by disordered BF_4^- anions. Protonation of the pyridine N atom is likely to be influential in establishing the planarity of the molecule, permitting the formation of an additional six-membered ring. The proton bonded to the pyridine N atom is disordered between the two rings with site occupancy factors of 0.70 and 0.30, respectively.

Comment

There has been extensive study directed towards understanding the chemistry of transition-metal complexes of 2,2′-bipyridine and bipyridine-like molecules because of their potential in photocatalysis and in the formation of metal-containing extended structures. A particularly interesting molecule in this category is the ligand di-2-pyridyl ketone (DPK), which has been shown by X-ray structural studies to undergo hydration to form a diol function, thus replacing the ketone, when in aqueous media and in the presence of a transition-metal cation (Wang, Richardson, Briggs, Jacobson & Jensen, 1986). The primary mode of coordination observed for DPK in its hydrated form is through the two pyridine N atoms and one O atom from the newly formed diol; thus, DPK becomes a tridentate ligand.

A second mode of coordination has been reported for DPK hydrate, where the ligand bridges two metal cations. Specifically, DPK has been shown to undergo hydration and bridge two Cu^{2+} cations such that the two trigonal bipyramidal coordination spheres around each Cu share a common edge (Basu, Bhaduri, Sapre & Jones, 1987).

In either mode, hydration occurs at the carbonyl function to facilitate coordination of the molecule. We present here the first two examples of DPK, characterized in the solid state, where hydration has not occurred.

catena-Poly[(*nitrato-O,O'*)*silver*(I)-*μ*-(*di-2-pyridyl ketone-N*:*N'*)] (I). A structural analysis of this complex was motivated by our continued interest in observing the behavior of DPK in aqueous media combined with metals that are not customarily stabilized by an octahedral coordination sphere (Sommerer & Abboud, 1993). Thus, silver(I) was chosen because either linear or tetrahedral geometry is usually observed for this species.

The crystals were found to consist of $Ag(DPK)^+$ repeating units, in which Ag^+ attains a distorted tetrahedral coordination environment. The DPK ligand bridges separate Ag^+ cations by coordinating through the pyridine N atoms, which results in an angle of 150.2 (1)° at the Ag^+. There is clearly no involvement of the carbonyl O atom with the Ag^+. The final two coordination sites of Ag^+ are occupied by O atoms from a nitrate anion, forming an angle of 49.4 (1)° at the metal center. The Ag^+—N distances are in good agreement with those previously observed (Nilsson & Oskarsson, 1982); however, there is a notable difference of 0.14 (4) Å in the two Ag^+—O distances associated with the nitrate anion. This difference in bond distances is only slightly longer than the difference of 0.12 (3) Å observed for the structurally similar (nitrato-*O,O'*)bis(4-nitropyridine *N*-oxide-*O*)silver(I) complex (Aoyama, Yamanaka, Ohba & Saito, 1990).

Di-2-pyridyl ketone (II). The crystals were found to contain monoprotonated DPK molecules balanced by disordered BF_4^- anions. Clearly, there was no evidence of either Nd^{3+} or NO_3^- in the crystal structure or the subsequent optical characterization of this species. The DPK molecule is almost planar, with a maximum variation of ± 0.17 Å (mean deviation 0.08 Å) for a least-squares plane calculated for the molecule. However, the planar pyridine rings appear to have rotated away from each other at the C6—C7 and C6—C5 bonds, as evidenced by the formation of a 8.3 (1)° dihedral angle and a torsion angle of −8.1 (2)° for N2—C7—C5—N1. Protonation of the pyridine N atom is likely to be quite influential in establishing the planarity of the molecules, since it permits the formation of an additional six-membered ring. The proton bonded to the pyridine N atom was found to be disordered between the two rings with site occupancy factors of 0.70 and 0.30 for H1*a* and H2*a*, respectively. Bond distances and angles were quite regular within the molecule, with average C—C distances of 1.366 (5) and 1.369 (4) Å, respectively, for the two pyridine rings. The BF_4^- anion, which balances the positively charged DPK, is disordered along its threefold axis, *i.e.* the B—F1 bond.

The DPK Ligand. These two structures provide a unique comparison of non-hydrated DPK; namely, first (I) where the molecule is perturbated by a metal cation, and secondly (II) where it is not. The distinguishing feature of DPK in the two structures is the

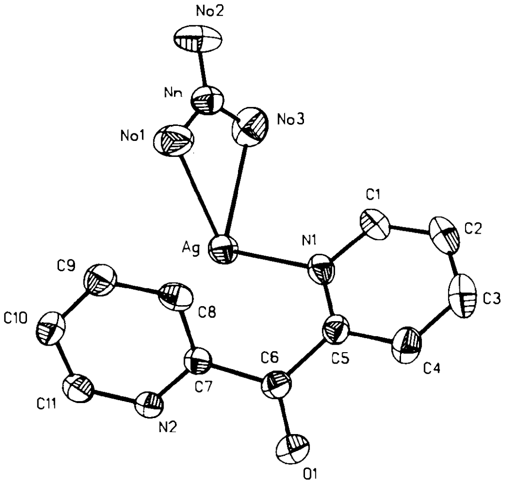

Fig. 1. Thermal ellipsoid drawing of (I) with ellipsoids drawn at the 50% probability level.

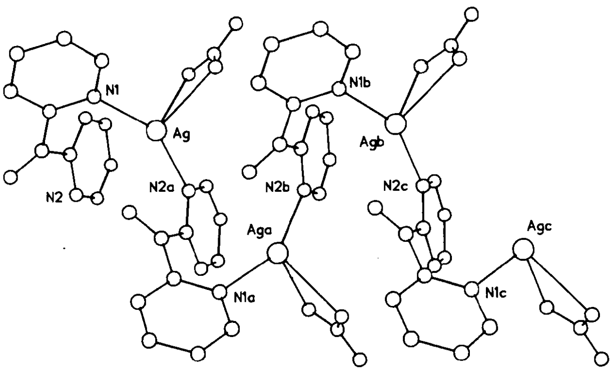

Fig. 2. Representation of the extended structure of (I). The symmetry operation for Ag*a*, N1*a*, N2*a* from Ag, N1, N2 is $x, \frac{1}{2} - y, \frac{1}{2} + z$; for Ag*b*, N1*b*, N2*b* from Ag, N1, N2 is $x, y, 1 + z$; and for Ag*c*, N1*c*, N2*c* from Ag, N1, N2 is $x, \frac{1}{2} - y, \frac{3}{2} + z$.

dramatic rotation of the pyridine rings around the C5—C6 and C7—C6 bonds in (I) *versus* (II). This rotation leads to a complete break of planarity of DPK in (I), resulting in a dihedral angle of 111.3 (2) *versus* 8.3 (1)$^\circ$ (II). There is little variation in the C5—C6 and C7—C6 bond lengths [1.498 (7) and 1.497 (7) Å, respectively for (I), and 1.508 (4) and 1.493 (4) Å, respectively for (II)] accompanying this break from planarity. Moreover, the coordination of the pyridine N atom to the metal cation in (I) appears to have no effect on the lengths of these bonds even though the planarity of the molecule is totally disrupted.

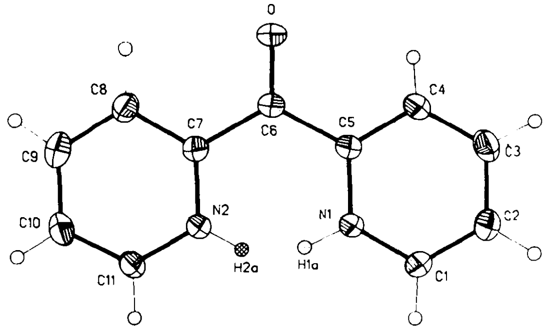

Fig. 3. Thermal ellipsoid drawing of (II) with ellipsoids drawn at the 50% probability level.

Experimental

Compound (I)

Crystal data

$[Ag(NO_3)(C_{11}H_8N_2O)]$
$M_r = 354.1$
Monoclinic
$P2_1/c$
$a = 8.687\ (1)$ Å
$b = 20.976\ (3)$ Å
$c = 7.035\ (1)$ Å
$\beta = 110.80\ (1)^\circ$
$V = 1198.4\ (3)$ Å^3
$Z = 4$
$D_x = 1.963$ Mg m^{-3}
$D_m = 1.98$ Mg m^{-3}
Density measured by flotation
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 50 reflections
$\theta = 10\text{-}11^\circ$
$\mu = 1.76$ mm^{-1}
$T = 298$ K
Blocks
0.44 × 0.30 × 0.24 mm
Colourless

Data collection

Siemens *P3m/V* diffractometer
ω-scans
Absorption correction: analytical
$T_{min} = 0.551$, $T_{max} = 0.704$
4807 measured reflections
2133 independent reflections
1819 observed reflections
$[I_{net} > 2.5\sigma(I_{net})]$
$R_{int} = 0.0153$
$\theta_{max} = 25^\circ$
$h = -10 \rightarrow 9$
$k = 0 \rightarrow 24$
$l = 0 \rightarrow 8$
4 standard reflections monitored every 96 reflections
intensity variation: <3%

Refinement

Refinement on F
$R = 0.035$
$wR = 0.032$
$S = 1.77$
1819 reflections
196 parameters
Only coordinates of H atoms refined
$w = 1/\sigma^2(F_{obs})$
$(\Delta/\sigma)_{max} = 0.1$
$\Delta\rho_{max} = 0.34$ e Å^{-3}
$\Delta\rho_{min} = -0.65$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Data collection and reduction and cell refinement: *SHELXTL-Plus* (Sheldrick, 1991). Program(s) used to solve and refine structure: *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *NRCVAX*.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *for* (I)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Ag	0.81080 (5)	0.66273 (2)	0.15298 (6)	0.052 (2)
O1	0.9673 (5)	0.7240 (2)	0.7961 (6)	0.074 (2)
N1	0.9885 (5)	0.6158 (2)	0.4339 (6)	0.043 (2)
N2	0.6669 (5)	0.7512 (2)	0.4965 (5)	0.042 (2)
C1	1.0920 (6)	0.5710 (2)	0.4062 (9)	0.050 (2)
C2	1.2173 (7)	0.5451 (2)	0.5637 (9)	0.058 (3)
C3	1.2391 (7)	0.5634 (3)	0.7571 (9)	0.064 (3)
C4	1.1387 (7)	0.6090 (3)	0.7871 (8)	0.055 (3)
C5	1.0141 (5)	0.6350 (2)	0.6231 (7)	0.040 (2)
C6	0.9097 (6)	0.6877 (2)	0.6562 (7)	0.047 (2)
C7	0.7319 (5)	0.6918 (2)	0.5234 (7)	0.036 (2)
C8	0.6380 (6)	0.6382 (2)	0.4451 (7)	0.047 (2)
C9	0.4692 (7)	0.6458 (2)	0.3386 (8)	0.053 (2)
C10	0.4038 (6)	0.7072 (2)	0.3122 (8)	0.055 (2)
C11	0.5041 (7)	0.7570 (2)	0.3895 (8)	0.052 (3)
NN	0.6930 (6)	0.5530 (2)	−0.1234 (6)	0.054 (2)
NO1	0.6171 (5)	0.5783 (2)	−0.0255 (7)	0.092 (3)
NO2	0.6361 (6)	0.5084 (2)	−0.2332 (6)	0.087 (3)
NO3	0.8317 (5)	0.5765 (2)	−0.1013 (6)	0.080 (2)

Table 2. *Geometric parameters* (Å, °) *for* (I)

Ag—N1	2.256 (4)	N1—C1	1.361 (6)
Ag—N2^i	2.249 (4)	N1—C5	1.332 (6)
C4—C5	1.384 (7)	C1—C2	1.361 (8)
C3—C4	1.360 (8)	C2—C3	1.360 (10)
C5—C6	1.498 (7)	C6—C7	1.497 (7)
N2—C7	1.354 (5)	O1—C6	1.203 (6)
C7—C8	1.382 (6)	N2—C11	1.351 (7)
C9—C10	1.394 (7)	C8—C9	1.399 (7)
Ag—NO1	2.458 (4)	C10—C11	1.344 (7)
NN—NO1	1.231 (6)	Ag—NO3	2.596 (4)
NN—NO3	1.260 (6)	NN—NO2	1.202 (6)
N1—C5—C4	121.1 (4)	N1—C5—C6	118.9 (4)
N1—Ag—N2^i	150.2 (1)	C4—C5—C6	119.9 (4)
N1—Ag—NO1	105.3 (2)	N1—Ag—NO3	96.1 (1)
N2^i—Ag—NO1	99.6 (2)	N2^i—Ag—NO3	112.6 (1)
O1—C6—C5	119.6 (4)	N2—C7—C8	122.3 (4)
Ag—N1—C1	117.2 (3)	Ag—N1—C5	124.2 (3)
C1—N1—C5	117.9 (4)	Ag—N2^i—C7^i	122.6 (3)
C7—C8—C9	118.7 (4)	Ag—N2^i—C11^i	119.4 (3)
C7—N2—C11	117.6 (4)	C8—C9—C10	118.4 (4)
N1—C1—C2	122.5 (5)	C9—C10—C11	119.3 (5)
N2—C11—C10	123.7 (5)	C1—C2—C3	119.3 (5)
NO1—NN—NO2	121.1 (5)	C2—C3—C4	118.9 (5)
NO1—NN—NO3	116.2 (4)	NO2—NN—NO3	122.8 (5)
Ag—NO1—NN	101.0 (3)	Ag—NO3—NN	93.4 (3)
C3—C4—C5	120.2 (5)	NO3—Ag—NO1	49.4 (1)

Symmetry code: (i) $x, \frac{3}{2} - y, \frac{1}{2} + z$.

Compound (II)

Crystal data

$C_{11}H_9N_2O^+.BF_4^-$
$M_r = 272.01$
Monoclinic
$P2_1/c$
$a = 12.314\ (2)$ Å
$b = 13.402\ (2)$ Å
$c = 7.212\ (1)$ Å
$\beta = 97.16\ (1)^\circ$
$V = 1180.9\ (3)$ Å^3
$Z = 4$

$D_x = 1.530$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 50 reflections
$\theta = 10\text{-}11^\circ$
$\mu = 0.14$ mm^{-1}
$T = 293$ K
Plates
$0.36 \times 0.30 \times 0.21$ mm
Yellow

Data collection

Siemens *P3m/V* diffractometer
ω scans
Absorption correction: analytical
$T_{\min} = 0.947$, $T_{\max} = 0.970$
2977 measured reflections
2725 independent reflections
1461 observed reflections $[F > 4\sigma(F)]$

$R_{\rm int} = 0.0119$
$\theta_{\max} = 27.5^\circ$
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 17$
$l = -9 \rightarrow 9$
4 standard reflections monitored every 96 reflections
intensity variation: <1%

Refinement

Refinement on F
$R = 0.0526$
$wR = 0.0597$
$S = 1.87$
1461 reflections
241 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F) + 0.0004F]^2$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.21$ e Å^{-3}
$\Delta\rho_{\min} = -0.19$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Data collection and reduction and cell refinement: *SHELXTL-Plus* (Sheldrick, 1991). Program(s) used to solve structure: *SHELXTL-Plus* (direct methods). Program(s) used to refine structure: *SHELX76* (Sheldrick, 1976) (full-matrix least squares). Geometric and parameter tables: *FUER* (Larson, 1993). Molecular graphics: *SHELXTL-Plus*.

Table 3. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *for* (II)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
O	0.1264 (2)	0.8044 (2)	−0.7140 (4)	0.0919 (8)
N1	0.2115 (2)	1.0428 (2)	−0.5452 (3)	0.0535 (8)
N2	0.3658 (2)	0.9081 (2)	−0.4722 (3)	0.0555 (8)
C1	0.1810 (3)	1.1380 (2)	−0.5417 (5)	0.0664 (11)
C2	0.0822 (3)	1.1665 (3)	−0.6346 (5)	0.0711 (12)
C3	0.0162 (3)	1.0975 (3)	−0.7292 (5)	0.0698 (12)
C4	0.0497 (2)	1.0003 (2)	−0.7316 (5)	0.0633 (10)
C5	0.1489 (2)	0.9728 (2)	−0.6380 (4)	0.0506 (9)
C6	0.1880 (2)	0.8661 (2)	−0.6369 (4)	0.0563 (9)
C7	0.2977 (2)	0.8358 (2)	−0.5421 (4)	0.0498 (9)
C8	0.3267 (3)	0.7360 (2)	−0.5318 (4)	0.0585 (10)
C9	0.4299 (3)	0.7122 (3)	−0.4511 (5)	0.0675 (13)
C10	0.5001 (3)	0.7856 (3)	−0.3813 (5)	0.0676 (12)
C11	0.4654 (2)	0.8822 (2)	−0.3925 (4)	0.0639 (10)
B	0.7227 (3)	0.9345 (3)	0.0468 (6)	0.0668 (14)
F1	0.6552 (2)	0.9168 (2)	0.1813 (3)	0.1155 (10)
F2	0.6656 (4)	0.9796 (7)	−0.1011 (7)	0.126 (3)
F3	0.7912 (4)	1.0081 (5)	0.1272 (7)	0.111 (2)
F4	0.7698 (11)	0.8579 (4)	0.002 (2)	0.207 (6)
F12	0.747 (2)	1.0194 (7)	0.000 (4)	0.264 (14)
F13	0.8224 (7)	0.8948 (14)	0.101 (2)	0.153 (8)
F14	0.6900 (9)	0.8732 (15)	−0.1006 (15)	0.146 (7)

Table 4. *Geometric parameters* (Å, °) *for* (II)

N1—C1	1.331 (4)	N1—C5	1.340 (4)
C4—C5	1.370 (4)	C1—C2	1.369 (5)
C3—C4	1.368 (5)	C2—C3	1.358 (5)
C5—C6	1.508 (4)	C6—C7	1.493 (4)
N2—C7	1.338 (3)	O—C6	1.209 (3)
C7—C8	1.384 (4)	N2—C11	1.335 (4)
C9—C10	1.364 (5)	C8—C9	1.368 (4)
F1—B	1.375 (5)	C10—C11	1.361 (5)
F2—B	1.346 (7)	F3—B	1.378 (7)
F4—B	1.242 (10)	F12—B	1.23 (2)
F13—B	1.350 (11)	F14—B	1.363 (15)
N1—C5—C4	118.6 (2)	N1—C5—C6	119.9 (2)
C4—C5—C6	121.5 (2)	O—C6—C5	117.6 (2)
N2—C7—C8	122.4 (2)	C1—N1—C5	122.4 (2)
C7—C8—C9	117.8 (2)	C7—N2—C11	118.2 (3)
C8—C9—C10	120.1 (3)	N1—C1—C2	119.6 (3)
C9—C10—C11	119.0 (3)	N2—C11—C10	122.5 (3)
C1—C2—C3	119.7 (3)	C2—C3—C4	119.6 (3)
C3—C4—C5	120.1 (3)	F1—B—F2	109.5 (3)
F1—B—F3	102.6 (4)	F2—B—F3	104.1 (5)
F2—B—F4	112.3 (7)	F3—B—F4	114.8 (7)
F4—B—F1	112.6 (6)	F1—B—F12	122.7 (8)
F1—B—F13	109.8 (6)	F12—B—F13	101 (1)
F12—B—F14	113.6 (9)	F13—B—F14	99.0 (9)
F14—B—F1	107.5 (6)		

Compound (I) was prepared as follows: silver nitrate was combined in a 1:2 stoichiometric ratio with DPK in 70 mL of H_2O. The resulting mixture was filtered and slow evaporation of the yellow filtrate gave clear yellow crystals suitable for X-ray diffraction studies. Although this complex was isolated from aqueous media, we found that hydration did not occur across the carbonyl since the IR spectrum of the solid product revealed the presence of a strong absorption band at 1690 cm^{-1}. Nonetheless, DPK still demonstrated an ability to bridge separate Ag^+ cations by coordinating through the two pyridyl N atoms and the result of this chemistry was a non-cross-linked metal containing an extended structure, as shown in the two thermal ellipsoid drawings of (I) (Figs. 1 and 2).

The isolation and subsequent structural solution of (II) was indeed serendipitous. Single crystals of this species were isolated from an aqueous solution of $Nd(NO)_3$:DPK (1:4), to which excess $NaBF_4$ had been added. This chemistry was a modification of a synthetic preparation which reported the isolation of lanthanide-DPK complexes, which was the original intent of the experiment (Jagannathan & Soundararajan, 1980). Clear pale-yellow crystals formed within 5 d and were the only X-ray diffraction quality crystals obtained from this experiment. A thermal ellipsoid drawing of (II) is shown in Fig. 3.

For (II), the ω-scan width was symmetrical over 1.2° about the $K\alpha_{1,2}$ maximum and the background was offset by 1.0 and −1.0 in ω from the $K\alpha_{1,2}$ maximum. The scan speed was varied within the range 3-6° min^{-1} (depending upon the intensity). The BF_4^- anion is disordered along the B—F1 bond; site occupancy factors are 0.65 (1) for F2, F3 and F4 and 0.35 (1) for F12, F13 and F14.

Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71420 (24 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1055]

References

Aoyama, T., Yamanaka, M., Ohba, S. & Saito, Y. (1990). *Acta Cryst.* C**46**, 762–766.

Basu, A., Bhaduri, S., Sapre, N. Y. & Jones, P. G. (1987). *J. Chem. Soc. Chem. Commun.* pp. 1724–1725.

Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–386.

Jagannathan, R. & Soundararajan, S. (1980). *Inorg. Nucl. Chem.* **42**, 145–147.

Larson, S. B. (1993). *FUER. Program for Geometric and Parameter Tables.* Personal communication.

Nilsson, K. & Oskarsson, A. (1982). *Acta Chem. Scand. Ser. A*, **36**, 605–610.

Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination.* Univ. of Cambridge, England.

Sheldrick, G. M. (1991). *SHELXTL-Plus.* Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sommerer, S. O. & Abboud, K. A. (1993). *Acta Cryst.* C**49**, 1152–1154.

Wang, S. L., Richardson, J. W., Briggs, S. J., Jacobson, R. A. & Jensen, W. P. (1986). *Inorg. Chim. Acta*, **111**, 67–72.

Acta Cryst. (1994). C**50**, 52–54

Inclusion Complex Between Uranyl and an Azacrown; Structure of $[UO_2(18\text{-azacrown-}6)]^{2+}.2CF_3SO_3^-$

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Abstract

The title complex, (1,4,7,10,13,16-hexaazacyclooctadecane)dioxouranium bis(trifluoromethylsulfonate), $[UO_2(C_{12}H_{30}N_6)]^{2+}.2CF_3SO_3^-$, is composed of $[UO_2(18\text{-azacrown-}6)]^{2+}$ and $CF_3SO_3^-$ ions. In the cation, the uranyl is bonded to the six N atoms of the crown in a hexagonal bipyramidal coordination. This is the first reported uranyl hexaazacrown inclusion complex.

Comment

Complexation of the dioxouranium by macrocycles, particularly by crown ethers, has been widely studied (Folcher, Charpin, Costes, Keller & de Villardi, 1979; Fux, Lagrange & Lagrange, 1984; Brighli, Fux, Lagrange & Lagrange, 1985). Of particular interest has been the inclusion of the uranyl ion in macrocycles; however, the majority of structural studies concern complexes in which the crown ligand is linked to the uranyl ion *via* hydrogen bonds (Rogers, Bond, Hipple, Rollins & Henry, 1991; Deshayes, Keller, Lance, Nierlich & Vigner, 1993; Gutberlet, Dreissig, Luger, Bechthold, Maung & Knochel, 1989) and few structural studies show a direct uranyl–crown coordination (Navaza, Villain & Charpin, 1984; Dejean, Charpin, Folcher, Rigny, Navaza & Tsoucaris, 1987; Deshayes, Keller, Lance, Navaza, Nierlich & Vigner, 1993). The probability of the uranyl complexing in the crown cavity is increased by a judicious choice of the solvent–anion pair, which has to be poorly coordinating with respect to the uranyl. As part of our studies of uranyl–macrocycle complexes, we report here the structure of a uranyl–azacrown inclusion complex (18-azacrown-6; 1,4,7,10,13,16-hexaazacyclooctadecane).

As shown in Figs. 1 and 2, the structure consists of $[UO_2(\text{azacrown-}6)]^{2+}$ cations, in which the uranyl group is hexacoordinated by the six N atoms of the azacrown giving a hexagonal bipyramidal geometry about the U atom, and $(CF_3SO_3)^-$ anions. The uranyl bond length is normal [average U—O 1.75 (1) Å] but the O—U—O angle of 174.9 (5)° deviates significantly from linearity. The six N atoms are in a more or less puckered plane; the deviations from the mean least-squares plane are 0.04 (1), −0.24 (1), 0.59 (2), −0.78 (2), 0.52 (2), −0.13 (2) Å for N(1), N(4), N(7), N(10), N(13), N(16), respectively, with the U atom at 0.066 (1) Å from this plane. The average U—N bond length of 2.66 (6) Å is longer than the average U—N distance of 2.54 (4) Å in a uranyl pentaporphyrin complex with five N atoms equatorially bonded to the U atom (Burrel, Hemmi, Lynch & Sessler, 1991), but compares well with the average U—N distance of 2.63 (8) Å in a pyrrole-derived uranyl Shiff base complex where six atoms are equatorially bonded (Sessler, Mody & Lynch, 1992). The average U—N bond length, which is longer than the analogous U—O distances in similar crown ether complexes [2.51 (2) Å (Navaza, Villian & Charpin, 1984) and 2.58 (7) Å (Deshayes, Keller, Lance, Navaza, Nierlich & Vigner, 1993)], indicates the relative weakness of the U—N bond compared with the U—O bond.

The macrocycle adopts a distorted $g-g+g+g-g+g+$ conformation, one of the six sequences