

strong interaction. The  $\nu_{C-O}$  of the thiobenzoate moiety in the IR spectrum of  $Ni(mtb)_2(diphos)$  occurs at 1590 and 1580  $cm^{-1}$  whereas in  $Ni_2(mtb)_4(C_2H_5OH)$  the  $\nu_{C-O}$  occurs at a much lower frequency of 1508  $cm^{-1}$  due to Ni–O bonding (Goodfellow & Stephenson, 1980).

The Ni–P distances observed in the present complex are shorter than the distances observed in similar compounds (Hope, Olmstead, Power & Viggiano, 1984). Tetrahedral geometry is observed around P atoms and the angles are close to 109° and the P–C distances are normal. The P(1)–C(1)–C(2)–P(2) dihedral angle is –45 (1)° indicating a puckered nature to maintain a planar  $NiS_2P_2$  chromophore. The average S–C bond distance, 1.734 (17) Å, is shorter than the single-bond distance of 1.832 (6) Å (Rout, 1982), indicating a partial delocalization of electrons over the O–C–S moiety. The phenyl rings are planar within 0.01 Å and other bond parameters are normal. There are no significant short contacts. The molecules in the unit cell are held together by van der Waals forces. The present crystal structure confirms the chromophore to be  $NiS_2P_2$  and shows that only S coordination in the parent complex is retained on interaction with diphos.

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### (1-2:5-6- $\eta$ -Cycloocta-1,5-diene)(2,4-dinitrophenyl)(4-methoxyphenyl)platinum(II) (1) and (1-2:5-6- $\eta$ -Cycloocta-1,5-diene)(2,4-dinitrophenyl)(4-nitrophenyl)platinum(II) (2)

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**Abstract.** (1):  $[Pt(C_6H_3N_2O_4)(C_7H_7O)(C_8H_{12})]$ , triclinic,  $P\bar{1}$ ,  $a = 6.872$  (4),  $b = 11.742$  (4),  $c = 13.582$  (5) Å,  $\alpha = 71.94$  (4),  $\beta = 76.55$  (5),  $\gamma = 75.25$  (3)°,  $V = 993.4$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.93$  g cm<sup>-3</sup>,  $\lambda(Mo K\alpha) = 0.71069$  Å,  $\mu = 67.99$  cm<sup>-1</sup>,  $F(000) = 560$ ,  $T = 295$  K,  $R = 0.039$  for 3253 observed reflections. (2):  $[Pt(C_6H_3N_2O_4)(C_6H_4NO_2)(C_8H_{12})]$ ,  $M_r = 592.5$ , triclinic,  $P\bar{1}$ ,  $a = 12.758$  (4),  $b = 11.213$  (4),  $c = 7.060$  (2) Å,  $\alpha = 77.570$  (3),  $\beta = 87.44$  (3),  $\gamma = 89.32$  (5)° (the Delaunay reduced cell is 11.213, 11.895, 12.758 Å, 90.88, 90.68, 144.58°),  $V = 985.3$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 2.00$  g cm<sup>-3</sup>,  $\lambda(Mo K\alpha) = 0.71069$  Å,  $\mu = 68.61$  cm<sup>-1</sup>,  $F(000) = 572$ ,  $T = 295$  K,  $R = 0.039$  for 3676 observed reflections. In (1) and (2) C(10) and C(20) of the phenyl rings, the Pt atom and

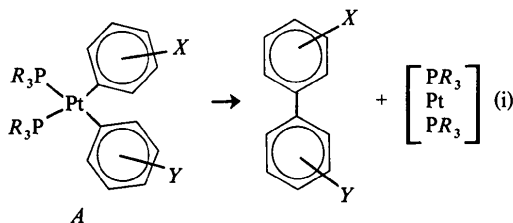
the midpoints of the coordinated double bonds C(1)=C(2) and C(5)=C(6) are nearly coplanar, the largest deviation from the plane being less than 0.11 Å. In (1) the angle between this plane and the 2,4-dinitrophenyl ring is 81.1°, while it is 86.9° between this plane and the 4-methoxyphenyl ring; in (2) the angles between the above-defined plane and the 2,4-dinitrophenyl or the 4-nitrophenyl ring measure 82.8 and 81.1° respectively (the mean standard deviation for all interplanar angles is 0.9°). In (1) the *ortho*-nitro group is twisted by 12.3° with respect to the phenyl ring, whereas this angle is 29.1° for the *para*-nitro group. In (2) all three nitro groups are nearly coplanar with the phenyl rings to which they are attached; the deviations are 5.9 [N(13)], 8.3 [N(15)] and 6.8° [N(23)]. A structure

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comparison between (1) and (2) gives no indication of a donor–acceptor interaction between the phenyl rings in (1).

**Introduction.** Kinetic studies of the reductive elimination (i) of the biphenyl system from compounds of the type *A* have revealed that these regiospecific



pericyclic reactions (Braterman, Cross & Young, 1977; Brune & Ertl, 1980; Brune, Ertl, Grafl & Schmidtberg, 1982) are characterized by unusually low activation enthalpies when the electron density in one of the two phenyl rings is enhanced by substituents with donor function, while it is simultaneously reduced in the second phenyl ring by electron-acceptor substituents; these small activation enthalpies are coupled with markedly negative activation entropies (Bayer & Brune, 1983). From these observations it was concluded that the transition state of the elimination (i) might be stabilized by a donor–acceptor interaction between the two *cis*-configured phenyl rings. We were interested whether such a donor–acceptor interaction could be observed in the structure of *A*. Long wavelength absorptions in the electronic spectra gave some indication that this might be the case (Stapp, 1985). Hence we synthesized the compounds (1-2:5-6- $\eta$ -cycloocta-1,5-diene)(2,4-dinitrophenyl)(4-methoxyphenyl)-platinum(II) (1) and (1-2:5-6- $\eta$ -cycloocta-1,5-diene)(2,4-dinitrophenyl)(4-nitrophenyl)platinum(II) (2) (Brune, Stapp & Schmidtberg, 1986). In (1) the strong electron acceptor 2,4-dinitrophenyl is *cis*-configured to the potential electron donor 4-methoxyphenyl allowing the possibility of a donor–acceptor interaction between the two ligands. In (2), with two acceptor-substituted phenyl rings, it was expected that no such interaction would occur.\*

**Experimental.** Crystals of both title compounds crystallize with well developed faces; both crystals were nearly parallelepipeds with a size *ca* 0.3 × 0.3 × 0.5 mm. 3809 for (1) and 4217 reflections for (2), Philips PW 1100 four-circle diffractometer, Mo *K* $\alpha$  radiation, graphite monochromator,  $\theta$ -2 $\theta$  scan,  $2\theta_{\max} = 50^\circ$ ,

\* (1-2:5-6- $\eta$ -Cycloocta-1,5-diene)[4-(*N,N*-dimethylamino)phenyl](2,4-dinitrophenyl)platinum(II) would have been more suitable for the study of a possible donor–acceptor interaction but this compound is unstable and spontaneously eliminates 4'-(*N,N*-dimethylamino)-2,4-dinitrobiphenyl even at room temperature.

3253 observed reflections for (1) [ $F > 1.5\sigma(F)$ ,  $-7 < h < 8$ ,  $-12 < k < 13$ ,  $0 < l < 15$ ] and 3676 observed reflections for (2) [ $F > 1.5\sigma(F)$ ,  $-15 < h < 15$ ,  $-13 < k < 13$ ,  $0 < l < 8$ ]. The intensity of three monitor reflections did not vary during the period of measurement. The cell parameters were obtained from refinement of the  $\theta$  values of 25 reflections [ $9.0 < \theta < 15.0^\circ$  for (1) and  $8.0 < \theta < 14.0^\circ$  for (2)]. Empirical absorption correction (Walker & Stuart, 1983), minimum and maximum absorption coefficients 0.792 and 1.766 for (1) and 0.629 and 1.175 for (2) respectively. The

Table 1. Atomic coordinates and equivalent isotropic thermal parameters (in  $\text{\AA}^2$ ) with *e.s.d.*'s in parentheses

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U<sub>eq</sub></i>
<i>(a) Compound (1)</i>				
C(1)	1.2054 (16)	0.4787 (9)	0.1128 (3)	0.043 (12)
C(10)	0.9114 (12)	0.7096 (7)	0.3046 (6)	0.027 (9)
C(11)	1.0396 (15)	0.7943 (8)	0.2908 (7)	0.039 (11)
C(12)	0.9894 (14)	0.8805 (8)	0.3474 (3)	0.040 (11)
C(13)	0.8134 (14)	0.8818 (7)	0.4220 (7)	0.034 (10)
C(14)	0.6818 (13)	0.8030 (7)	0.4405 (6)	0.032 (9)
C(15)	0.7346 (13)	0.7225 (7)	0.3777 (6)	0.028 (9)
C(2)	1.0321 (16)	0.4271 (9)	0.1537 (7)	0.042 (12)
C(20)	0.9883 (14)	0.7138 (8)	0.0994 (7)	0.035 (10)
C(21)	1.0040 (16)	0.7963 (11)	0.0296 (8)	0.052 (13)
C(22)	0.9277 (17)	0.6837 (11)	−0.0572 (8)	0.056 (14)
C(23)	0.7337 (17)	0.8903 (9)	−0.0728 (7)	0.045 (12)
C(23')	0.4702 (19)	0.9900 (12)	−0.1790 (10)	0.065 (16)
C(24)	0.6156 (15)	0.8116 (9)	−0.0041 (8)	0.043 (12)
C(25)	0.6949 (16)	0.7226 (9)	0.0825 (8)	0.044 (12)
C(3)	1.0225 (16)	0.3074 (9)	0.2396 (8)	0.044 (12)
C(4)	0.9539 (15)	0.3268 (8)	0.3522 (8)	0.042 (12)
C(5)	1.0307 (14)	0.4257 (8)	0.3708 (7)	0.036 (10)
C(6)	1.2226 (14)	0.4525 (8)	0.3321 (7)	0.037 (10)
C(7)	1.3972 (15)	0.3803 (10)	0.2707 (9)	0.052 (14)
C(8)	1.4101 (16)	0.4275 (10)	0.1507 (9)	0.053 (14)
N(13)	0.7600 (12)	0.9710 (7)	0.4840 (7)	0.042 (10)
N(15)	0.5793 (11)	0.6479 (6)	0.3931 (6)	0.035 (9)
O(13a)	0.6601 (12)	0.9456 (6)	0.5717 (6)	0.055 (10)
O(13b)	0.8195 (14)	1.0682 (7)	0.4440 (7)	0.073 (13)
O(15a)	0.5922 (11)	0.5898 (7)	0.3315 (6)	0.054 (10)
O(15b)	0.4428 (15)	0.6494 (10)	0.4661 (8)	0.093 (16)
O(23)	0.6731 (12)	0.9787 (7)	−0.1606 (6)	0.062 (10)
Pt(1)	1.0048 (1)	0.5823 (1)	0.2223 (1)	0.027 (1)
<i>(b) Compound (2)</i>				
C(1)	0.3719 (6)	0.5108 (6)	−0.2064 (12)	0.048 (7)
C(10)	0.2046 (5)	0.1880 (6)	−0.1456 (9)	0.035 (5)
C(11)	0.2242 (6)	0.1186 (6)	0.0422 (10)	0.042 (6)
C(12)	0.1842 (6)	0.0008 (7)	0.1116 (10)	0.044 (6)
C(13)	0.1293 (5)	−0.0505 (6)	−0.0160 (10)	0.036 (6)
C(14)	0.1076 (5)	0.0090 (6)	−0.2011 (9)	0.035 (5)
C(15)	0.1458 (5)	0.1287 (6)	−0.2591 (9)	0.035 (5)
C(2)	0.3143 (6)	0.5489 (7)	−0.3702 (12)	0.047 (7)
C(20)	0.3863 (5)	0.2733 (6)	−0.3539 (11)	0.042 (6)
C(21)	0.4661 (6)	0.2100 (9)	−0.2504 (12)	0.056 (8)
C(22)	0.5460 (6)	0.1518 (9)	−0.3385 (13)	0.059 (9)
C(23)	0.5446 (6)	0.1610 (7)	0.5360 (12)	0.047 (7)
C(24)	0.4665 (6)	0.2230 (8)	0.6461 (11)	0.055 (8)
C(25)	0.3870 (6)	0.2790 (8)	0.5580 (11)	0.049 (7)
C(3)	0.2201 (7)	0.6356 (7)	0.3843 (14)	0.058 (8)
C(4)	0.1142 (6)	0.5668 (7)	0.3449 (13)	0.054 (8)
C(5)	0.1148 (6)	0.4543 (7)	0.1818 (11)	0.045 (7)
C(6)	0.1663 (6)	0.4371 (7)	0.0098 (12)	0.048 (7)
C(7)	0.2289 (7)	0.5362 (8)	−0.0551 (13)	0.057 (8)
C(8)	0.3467 (7)	0.5400 (8)	0.0070 (13)	0.060 (9)
N(13)	0.0882 (5)	−0.1751 (6)	−0.0510 (10)	0.048 (6)
N(15)	0.1181 (5)	0.1919 (6)	0.4549 (9)	0.047 (6)
N(23)	0.6273 (6)	0.1029 (7)	0.6326 (12)	0.046 (7)
O(13a)	0.0453 (5)	−0.2227 (5)	0.0649 (10)	0.067 (7)
O(13b)	0.0989 (5)	−0.2263 (5)	−0.2208 (9)	0.069 (7)
O(15a)	0.0767 (7)	0.1333 (6)	0.5580 (9)	0.093 (9)
O(15b)	0.1375 (5)	0.2997 (5)	0.5129 (8)	0.063 (6)
O(23a)	0.6305 (6)	0.1200 (8)	0.8066 (12)	0.096 (10)
O(23b)	0.6897 (6)	0.0390 (8)	0.5338 (12)	0.090 (9)
Pt(1)	0.2682 (1)	0.3564 (1)	0.2278 (1)	0.034 (1)

Table 2. *Interatomic distances (Å) and angles (°) with e.s.d.'s in parentheses*

C(1)—C(2)	1.395 (18)	1.384 (12)	C(2)—Pt(1)	2.245 (12)	2.250 (8)	C(6)—C(7)	1.520 (17)	1.535 (13)
C(1)—C(8)	1.523 (15)	1.532 (14)	C(20)—C(21)	1.393 (16)	1.378 (11)	C(6)—Pt(1)	2.295 (7)	2.297 (9)
C(1)—Pt(1)	2.218 (12)	2.227 (8)	C(20)—C(25)	1.374 (15)	1.428 (12)	C(7)—C(8)	1.540 (16)	1.545 (14)
C(10)—C(11)	1.432 (15)	1.417 (9)	C(20)—Pt(1)	2.048 (7)	2.032 (8)	N(13)—O(13a)	1.230 (13)	1.220 (11)
C(10)—C(15)	1.387 (14)	1.394 (11)	C(21)—C(22)	1.407 (12)	1.398 (13)	N(13)—O(13b)	1.218 (14)	1.225 (9)
C(10)—Pt(1)	2.023 (9)	2.021 (7)	C(22)—C(23)	1.378 (17)	1.376 (13)	N(15)—O(15a)	1.210 (13)	1.220 (11)
C(11)—C(12)	1.384 (16)	1.400 (11)	C(23)—C(24)	1.371 (16)	1.379 (12)	N(15)—O(15b)	1.197 (16)	1.214 (9)
C(12)—C(13)	1.386 (16)	1.387 (11)	C(24)—C(25)	1.421 (11)	1.380 (13)	O(23)—C(23')	1.439 (15)	
C(13)—C(14)	1.383 (15)	1.372 (9)	C(3)—C(4)	1.561 (16)	1.548 (12)	C(23)—O(23)	1.384 (10)	
C(13)—N(13)	1.466 (14)	1.470 (9)	C(4)—C(5)	1.499 (16)	1.514 (11)	C(23)—N(23)		1.454 (12)
C(14)—C(15)	1.391 (14)	1.403 (10)	C(5)—C(6)	1.379 (16)	1.382 (12)	N(23)—O(23a)		1.201 (13)
C(15)—N(15)	1.486 (14)	1.467 (9)	C(5)—Pt(1)	2.279 (8)	2.279 (8)	N(23)—O(23b)		1.206 (12)
C(2)—C(3)	1.529 (13)	1.530 (12)						
C(5)—Pt(1)—C(10)	92.5 (3)	94.0 (3)	C(11)—C(12)—C(13)	118.7 (11)	117.3 (6)	C(4)—C(5)—C(6)	125.8 (10)	128.2 (8)
C(6)—Pt(1)—C(10)	95.3 (3)	94.2 (3)	N(13)—C(13)—C(14)	117.6 (10)	117.1 (7)	C(6)—C(5)—Pt(1)	73.1 (5)	73.1 (5)
C(1)—Pt(1)—C(10)	158.5 (4)	156.3 (3)	C(12)—C(13)—C(14)	122.9 (10)	124.2 (6)	C(4)—C(5)—Pt(1)	105.2 (5)	105.3 (5)
C(2)—Pt(1)—C(10)	165.1 (4)	167.7 (3)	C(12)—C(13)—N(13)	119.5 (10)	118.7 (6)	C(5)—C(6)—C(7)	125.6 (10)	124.5 (7)
C(1)—Pt(1)—C(2)	36.4 (5)	36.0 (3)	C(13)—C(14)—C(15)	115.8 (10)	115.7 (7)	C(5)—C(6)—Pt(1)	71.8 (5)	71.7 (5)
C(10)—Pt(1)—C(20)	87.4 (3)	85.7 (3)	C(10)—C(15)—C(14)	125.9 (10)	125.0 (6)	C(7)—C(6)—Pt(1)	109.9 (6)	109.0 (5)
C(1)—Pt(1)—C(20)	90.6 (4)	91.8 (3)	C(14)—C(15)—N(15)	113.9 (9)	114.7 (6)	C(6)—C(7)—C(8)	114.2 (8)	114.5 (8)
C(2)—Pt(1)—C(20)	94.5 (4)	96.3 (3)	C(10)—C(15)—N(15)	120.2 (8)	120.3 (6)	C(1)—C(8)—C(7)	115.1 (11)	114.9 (8)
C(5)—Pt(1)—C(20)	161.6 (4)	161.6 (3)	C(1)—C(2)—C(3)	125.0 (9)	124.9 (8)	C(13)—N(13)—O(13a)	117.7 (10)	118.6 (6)
C(6)—Pt(1)—C(20)	163.2 (4)	163.2 (3)	C(1)—C(2)—Pt(1)	70.7 (7)	71.1 (4)	C(13)—N(13)—O(13b)	118.8 (9)	118.3 (7)
C(2)—Pt(1)—C(5)	81.1 (3)	80.3 (3)	C(3)—C(2)—Pt(1)	111.3 (7)	111.5 (5)	O(13a)—N(13)—O(13b)	123.5 (11)	123.1 (7)
C(1)—Pt(1)—C(5)	96.0 (3)	95.6 (3)	C(21)—C(20)—C(25)	117.8 (8)	117.9 (8)	C(15)—N(15)—O(15a)	119.6 (9)	118.5 (7)
C(5)—Pt(1)—C(6)	35.1 (4)	35.2 (3)	Pt(1)—C(20)—C(25)	121.3 (7)	119.2 (6)	C(15)—N(15)—O(15b)	118.1 (10)	120.4 (7)
C(1)—Pt(1)—C(6)	80.8 (3)	81.5 (3)	C(21)—C(20)—Pt(1)	120.9 (7)	122.8 (6)	O(15a)—N(15)—O(15b)	122.2 (11)	121.1 (7)
C(2)—Pt(1)—C(6)	87.2 (3)	87.4 (3)	C(20)—C(21)—C(22)	121.2 (11)	122.2 (8)	O(23)—C(23)—C(24)	124.5 (10)	
C(2)—C(1)—C(8)	125.0 (8)	125.7 (8)	C(21)—C(22)—C(23)	119.9 (12)	117.9 (8)	C(22)—C(23)—O(23)	115.5 (10)	
C(2)—C(1)—Pt(1)	72.9 (7)	72.9 (5)	C(22)—C(23)—C(24)	120.0 (8)	122.1 (8)	C(23)—O(23)—C(23')	117.4 (10)	
C(8)—C(1)—Pt(1)	107.6 (8)	106.5 (5)	C(23)—C(24)—C(25)	119.7 (10)	119.7 (8)	C(22)—C(23)—N(23)		119.4 (8)
C(11)—C(10)—C(15)	114.6 (9)	115.1 (6)	C(20)—C(25)—C(24)	121.4 (10)	120.1 (7)	C(23)—N(23)—O(23a)		118.9 (8)
Pt(1)—C(10)—C(15)	126.7 (7)	126.5 (5)	C(2)—C(3)—C(4)	112.8 (9)	112.5 (7)	C(23)—N(23)—O(23b)		119.4 (9)
C(11)—C(10)—Pt(1)	118.7 (7)	118.4 (6)	C(3)—C(4)—C(5)	115.9 (9)	114.4 (7)	O(23a)—N(23)—O(23b)		122.8 (9)
C(10)—C(11)—C(12)	121.9 (11)	122.6 (7)						

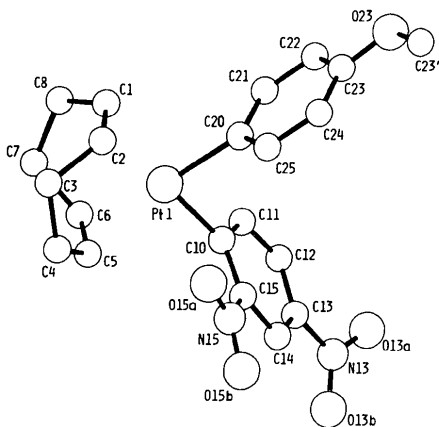


Fig. 1. Projection of compound (1).

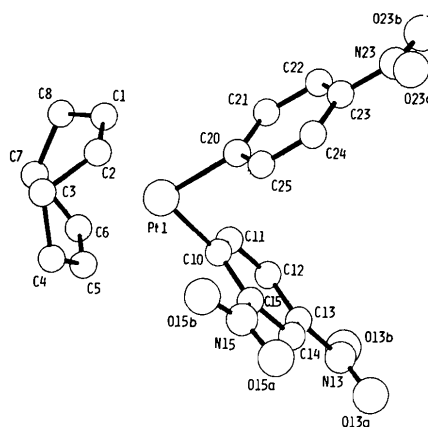


Fig. 2. Projection of compound (2).

structures were solved by Patterson methods and refined by full-matrix least squares (on  $F$ ) first with isotropic and then with anisotropic temperature parameters, using unit weights (Sheldrick, 1977), until the parameter shifts were less than the corresponding standard deviation. The H atoms were not located. Max. heights in difference Fourier map  $2.30$  for (1) and  $1.31 \text{ e } \text{Å}^{-3}$  for (2). Final  $R = 0.039$  for (1) and (2) for 3253 and 3676 observed reflections. The atomic scattering factors were from Cromer & Mann (1968) and Doyle & Turner (1968).

**Discussion.** Final atomic coordinates and equivalent isotropic thermal parameters are given in Table 1,\* interatomic distances and angles in Table 2. Figs. 1 and 2 show the structures of the molecules of (1) and (2) in a similar orientation and include atomic numbering. It

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43445 (39 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

is clear from the figures and tables that – as a comparison of the structures of (1) and (2) indicates – no interaction between C(10) and C(20) occurs. The observed kinetic phenomenon would therefore appear to be an effect only in the transition state of the elimination (i).

It has been spectroscopically established (Laube, 1984) that in the isolated molecules (in solution) the perpendicular orientation of the two phenyl rings with respect to the plane defined by square-planar Pt valences is the preferred conformation with a relatively deep potential hollow; as a consequence *E*, *Z* isomers of bis-*ortho*-substituted compounds have been detected (Laube, 1984). In the solid phase the phenyl rings in (1) and (2) deviate from this perpendicular orientation [81.9 and 86.9° in (1); 82.8 and 81.1° in (2)]; these distortions are probably caused by packing effects due to short intermolecular distances.

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## Actinide Structural Studies. 11.\* X-ray Study of a Possible Seven-Coordinate Uranyl Ion: Structure of (2,2'-Bipyridine *N,N'*-dioxide)dinitratodioxouranium(VI)

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**Abstract.** [UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>O<sub>2</sub>)], *M<sub>r</sub>* = 582.2, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 9.231 (5), *b* = 10.556 (7), *c* = 15.839 (5) Å, β = 96.99 (4)°, *V* = 1532 (1) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 2.52, *D<sub>m</sub>* = 2.3 (1) g cm<sup>-3</sup>, λ(Mo *K*α) = 0.71069 Å, μ = 101.1 cm<sup>-1</sup>, *F*(000) = 1072, *T* = 291 K, *R* = 0.063 for 1974 unique observed reflections. The title compound contains a [UO<sub>2</sub>]<sup>2+</sup> ion [U–O 1.76 (2) Å], coordinated by one 2,2'-bipyridine *N,N'*-dioxide [U–O 2.38 (1) Å] and two NO<sub>3</sub><sup>-</sup> groups [U–O 2.51 (1) Å]. Evidence is presented that the supposed seven-coordinate [UO<sub>2</sub>]<sup>2+</sup> ion in [UO<sub>2</sub>(bpyO<sub>2</sub>)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>].4H<sub>2</sub>O in reality exists as the six-coordinate [UO<sub>2</sub>(bpyO<sub>2</sub>)<sub>2</sub>(NO<sub>3</sub>)]<sup>+</sup> ion.

**Introduction.** A complex formed from uranyl nitrate and 2,2'-bipyridine *N,N'*-dioxide (bpyO<sub>2</sub>) was claimed by Madan & Chan (1977) from IR evidence to contain [UO<sub>2</sub>]<sup>2+</sup> ions coordinated by seven equatorial ligands, made up of two bidentate bpyO<sub>2</sub> groups, one bidentate and one unidentate nitrate. However, this conclusion seems suspect in view of the steric constraints around the [UO<sub>2</sub>]<sup>2+</sup> group, where even six ligands can only be

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fitted in if one or more short-bite bidentate ligands are present (Alcock, 1973). Furthermore, the identification of precisely how nitrate groups are coordinated from their IR spectrum is known to be uncertain (Cotton, Goodgame & Sonderberg, 1963). Two complexes can be formed in this system, depending on the precise preparative conditions: [UO<sub>2</sub>(bpyO<sub>2</sub>)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>] (1) (previously prepared by Ahuja & Singh, 1973) and [UO<sub>2</sub>(bpyO<sub>2</sub>)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>].4H<sub>2</sub>O (2) (as reported by Madan & Chan, 1977) and these have been investigated crystallographically.

**Experimental.** The preparative conditions for (1) and (2) are almost identical, except that for (1) the solution of bpyO<sub>2</sub> is reacted with solid uranyl nitrate, whereas (2) is formed from solutions of the reactants.

(1) was prepared by adding a solution of 2,2'-bipyridine *N,N'*-dioxide (8.5 mmol) in hot methanol (400 ml) to uranyl nitrate hexahydrate (4.2 mmol) in the solid state. The reaction mixture yielded a fine precipitate of the desired product on standing for a few hours. Crystals of a suitable size for X-ray diffraction studies were obtained by slow evaporation from a hot glacial acetic acid solution. The IR spectrum and the formula as obtained from X-ray structure analysis agree with those reported by Ahuja & Singh (1973).

\* Part 10: Alcock, Flanders & Brown (1986).

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