References

Aliev, A. E., Harris, K. D. M., Shannon, I. J., Glidewell, C., Zakaria, C. M. & Schofield, P. A. (1995). *J. Phys. Chem.* **99**, 12008–12015.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Enraf–Nonius (1992). *CAD-4-PC*. Version 1.1. Enraf–Nonius, Delft, The Netherlands.
Etter, M. C. (1990). *Acc. Chem. Res.* **23**, 120–126.
Etter, M. C., MacDonald, J. C. & Bernstein, J. (1990). *Acta Cryst.* B**46**, 256–262.
Ferguson, G., Gallagher, J. F., Glidewell, C., Low, J. N. & Scrimgeour, S. N. (1992). *Acta Cryst.* C**48**, 1272–1275.
Ferguson, G., Gallagher, J. F., Glidewell, C. & Zakaria, C. M. (1993*a*). *Acta Cryst.* C**49**, 967–971.
Ferguson, G., Gallagher, J. F., Glidewell, C. & Zakaria, C. M. (1993*b*). *J. Chem. Soc. Dalton Trans.* pp. 3499–3506.
Ferguson, G., Glidewell, C. & Patterson, I. L. J. (1996). *Acta Cryst.* C**52**, 420–423.
Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.
Glidewell, C., Ferguson, G., Lough, A. J. & Zakaria, C. M. (1994). *J. Chem. Soc. Dalton Trans.* pp. 1971–1982.
Seip, H. M. & Seip, R. (1973). *Acta Chem. Scand.* **27**, 4024–4027.
Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures.* University of Göttingen, Germany.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Spek, A. L. (1995*a*). *PLATON. Molecular Geometry Program.* Version of October 1995. University of Utrecht, The Netherlands.
Spek, A. L. (1995*b*). *PLUTON. Molecular Graphics Program.* Version of July 1995. University of Utrecht, The Netherlands.

Acta Cryst. (1996). C**52**, 3013-3016

Pentaammine-$2\kappa^5N$-(μ-4,4′-bipyridine-$1\kappa N$:$2\kappa N'$)(2,2′-bipyridine-$1\kappa^2N,N'$)-(2,2′:6′,2″-terpyridine-$1\kappa^3N,N',N''$)diruthenium Tetrakis(hexafluorophosphate) Acetonitrile Solvate

David J. Szalda,[a] Florencia Fagalde[b] and Néstor E. Katz[b]

[a]*Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973-5000, USA, and* [b]*Instituto de Quimica Fisica, Facultad de Bioquimica, Quimica y Farmacia, Universidad Nacional de Tucumán, Ayacucho 491, 4000 San Miguel de Tucumán, Argentina. E-mail: szalda@dynamics.chm.bnl.gov*

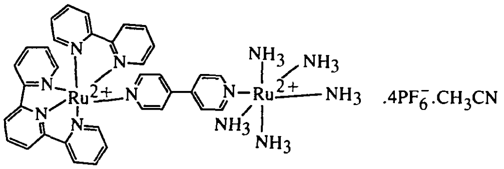
(*Received 13 June 1996; accepted 12 September 1996*)

Abstract

In the title compound, $[Ru_2(C_{10}H_8N_2)_2(C_{15}H_{11}N_3)(NH_3)_5](PF_6)_4.CH_3CN$, the bridging Ru—N bond length in the Ru(2,2′-bipyridine)(2,2′:6′,2″-terpyridine)(4,4′-bipyridine) moiety is 2.112 (7) Å, whereas that in the $Ru(NH_3)_5$(4,4′-bipyridine) moiety is 2.052 (7) Å. The difference arises from the fact that the $[Ru^{II}(NH_3)_5]^{2+}$ group is a stronger π-donor than the $[Ru^{II}$(2,2′-bipyridine)(2,2′:6′,2″-terpyridine)$]^{2+}$ moiety.

Comment

Ruthenium complexes of the tridentate 2,2′:6′2″-terpyridine (terpy) ligand and of the bidentate 2,2′-bipyridine (bpy) ligand are attractive as potential photocatalysts (Constable, 1986; Hecker, Gushurst & McMillin, 1991; Petersen, Morgan, Hsu, Billadeau & Ronco, 1991), powerful electrocatalysts for oxidation of organic substrates (Moyer, Thompson & Meyer, 1980; Thompson & Meyer, 1982; Binstead & Meyer, 1987), effective agents for DNA cleavage (Grover, Gupta, Singh & Thorp, 1992) and building blocks for supramolecular species (Collin *et al.*, 1991). In the course of our studies of mono- and dinuclear complexes (Fagalde & Katz, 1993, 1995) derived from the photosensitizing $[Ru^{II}(terpy)(bpy)]^{2+}$ unit, we have obtained crystals of the PF_6^- salt of the $[(terpy)(bpy)Ru^{II}(\mu\text{-}4,4'\text{-}bpy)Ru^{II}(NH_3)_5]^{4+}$ cation (where 4,4′-bpy is 4,4′-bipyridine), (1). These systems are important in mixed-valence chemistry (Creutz, 1983; Meyer, 1978) and structural data are necessary in the reorganizational energy calculations for intramolecular electron transfers.



(I)

An *ORTEP*III (Burnett & Johnson, 1996) drawing of (1) is shown in Fig. 1. The left-hand side of the molecule consists of an Ru atom coordinated to a 2,2′-bipyridine ligand, a 2,2′:6′,2″-terpyridine ligand and a 4,4′-bipyridine ligand which bridges the $[Ru(bpy)(terpy)]^{2+}$ and $[Ru(NH_3)_5]^{2+}$ metal centers. Both Ru atoms are in the +2 oxidation state. The asymmetric unit also contains four hexafluorophosphate anions, one of which is disordered. There is also one acetonitrile molecule of crystallization in the asymmetric unit which is also disordered. The acetonitrile molecule is disordered over at least two positions and displays weak hydrogen bonding with the ammine ligands and the anions in both positions. The hexafluorophosphate anions are also hydrogen bonded to the coordinated ammine ligands. The bond lengths and angles within the bipyridine and terpyridine ligands are normal. The $[Ru(bpy)(terpy)]^{2+}$—N(4,4′-bpy) bond length of 2.112 (7) Å is very similar to that observed in $[Ru(terpy)(bpy)(py)]^{2+}$ of 2.114 (6) Å (Hecker, Fanwick & McMillin, 1991). The $[Ru(NH_3)_5]^{2+}$—N(4,4′-bpy) bond length of 2.052 (7) Å is significantly longer than the Ru—N(pz) bond length (pz is pyrazine) of 2.006 (6) Å observed in

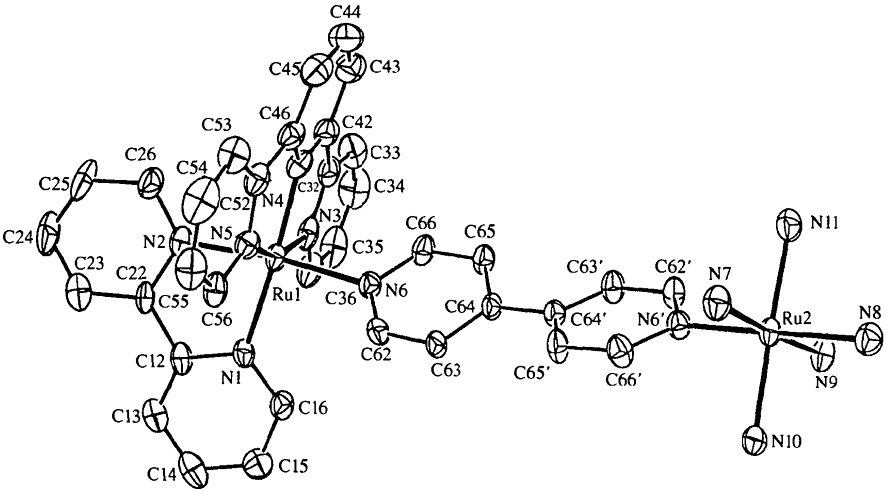


Fig. 1. An *ORTEPIII* (Burnett & Johnson, 1996) drawing of the $[(bpy)(terpy)Ru(\mu\text{-}4,4'\text{-}bpy)Ru(NH_3)_5]^{4+}$ cation. The displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

$[(NH_3)_5Ru(pz)]^{2+}$ (Gress, Creutz & Quicksall, 1981) and the Ru—N(mepz) bond length (mepz is methylpyrazine) of 1.95 (1) Å found in $[(NH_3)_5Ru(mepz)]^{3+}$ (Wishart, Bino & Taube, 1986). It is also longer than that found in $[(NH_3)_5Ru^{II}(pz)Ru^{II}(NH_3)_5]^{4+}$ of 2.013 (3) Å (Fürholz, Joss, Bürgi & Ludi, 1985) and in the Creutz–Taube complex $[(NH_3)_5Ru(pz)Ru(NH_3)_5]^{5+}$ of 1.991 (9) Å (Fürholz, Joss, Bürgi & Ludi, 1985), but shorter than the Ru—N(pz) bond length of 2.076 Å found in $[(NH_3)_5Ru^{III}(pz)]^{3+}$ (Gress, Creutz & Quicksall, 1981). These observations can be attributed to the stronger π-back-bonding interaction between Ru and pyrazine than between Ru and 4,4′-bipyridine.

In the title complex, the difference between the [Ru(terpy)(bpy)]—N(4,4′-bpy) bond length of 2.112 (7) Å and the $[Ru(NH_3)_5]$—N(4,4′-bpy) bond length of 2.052 (7) Å in the same complex can be explained by the fact that the $[Ru^{II}(NH_3)_5]$ group has stronger π-donor abilities than the $[Ru^{II}(terpy)(bpy)]$ moiety due to the competition between the bpy and terpy ligands for the π-electron density of Ru in $[Ru^{II}(terpy)(bpy)]$. The Ru1 atom lies 0.44 Å out of the plane of the attached pyridine ring (N6, C61–C66) of the bridging 4,4′-bpy ligand, while the Ru2 atom lies in the plane of its attached pyridine ring (N6′, C61′–C66′). This results in a bending of the Ru1—N(4,4′-bpy)—Ru2 backbone. The Ru1 atom lies 0.14 Å out of the plane defined by atoms N2, N3, N6 and N5, which is slightly tetrahedral, the N atoms being 0.25 Å above and below the plane. The associated pyridine ring of the bridging 4,4′-bpy ligand makes an angle of 45.1° with this plane. The Ru2 atom lies in the plane defined by atoms N6′, N7, N8 and N9, and the associated pyridine ring (N6′, C61′–C66′) of the bridging 4,4′-bpy ligand makes an angle of 43.0° with this plane.

It is well known that the 2,2′:6′2″-terpyridine ligand coordinates to ruthenium in a meridional fashion (Grover, Gupta, Singh & Thorp, 1992). The steric limitations typical of the metal–terpy moiety are reflected in the Ru—N bonds to the central N atom of terpy [1.949 (9) Å], which are shorter than the Ru—N bonds to the terminal N atom of terpy [2.076 (7) Å]. The N—Ru—N angle formed by the terminal terpy N atoms [158.7 (4)°] is typical (Leizing *et al.*, 1990). As found previously in $[Ru(terpy)(bpy)(py)]^{2+}$ (Hecker, Fanwick & McMillin, 1991), there is a difference in the two Ru—N bond lengths of the bpy ligand.

The twisting of the rings of the 4,4′-bpy ligand in (1) by 18° is consistent with the theoretical calculations on the mixed-valent ion $[(NH_3)_5Ru(4,4'\text{-}bpy)Ru(NH_3)_5]^{5+}$ (Woitellier, Launay & Joachim, 1989), which is a model system for molecular switching.

Experimental

Complex (1) was prepared as described previously (Fagalde & Katz, 1993). A sample (8 mg) was dissolved in 6 ml of an MeCN/toluene (1:1 *v*/*v*) solution, which was kept in the dark and left to evaporate slowly at room temperature for 5 d. The crystals obtained were washed with pentane and dried in air.

Crystal data

$[Ru_2(C_{10}H_8N_2)_2(C_{15}H_{11}N_3)$-
$(NH_3)_5](PF_6)_4.CH_3CN$
M_r = 1453.88
Monoclinic
$P2_1/n$
a = 8.7472 (7) Å
b = 34.341 (6) Å
c = 18.952 (2) Å
β = 97.854 (7)°
V = 5639 (1) Å^3
Z = 4
D_x = 1.712 Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 25 reflections
θ = 17–33°
μ = 6.53 mm^{-1}
T = 293 K
Needle
0.52 × 0.22 × 0.04 mm
Reddish–purple

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: *ABSOR CRYSNET* Gaussian (Berman, Bernstein, Bernstein, Koetzle & Williams, 1976)
$T_{\min} = 0.232$, $T_{\max} = 0.767$
8854 measured reflections
8247 independent reflections
4961 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int} = 0.045$
$\theta_{\max} = 60°$
$h = -2 \rightarrow 9$
$k = -7 \rightarrow 38$
$l = -20 \rightarrow 21$
3 standard reflections frequency: 60 min intensity decay: <1%

Refinement

Refinement on F^2
$R(F) = 0.066$
$wR(F^2) = 0.177$
$S = 1.07$
8239 reflections
740 parameters
H atoms placed in calculated positions
$w = 1/[\sigma^2(F_o^2) + (0.1491P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.32$
$\Delta\rho_{\max} = 1.22$ e Å^{-3}
$\Delta\rho_{\min} = -1.06$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

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

	x	y	z	$U_{\rm eq}$
Ru1	0.48359 (7)	0.12653 (2)	0.64102 (3)	0.0614 (2)
N1	0.5576 (8)	0.0704 (2)	0.6191 (4)	0.067 (2)
C12	0.5918 (10)	0.0651 (3)	0.5530 (5)	0.074 (3)
C13	0.6475 (12)	0.0301 (4)	0.5324 (6)	0.084 (3)
C14	0.6720 (13)	−0.0002 (4)	0.5803 (7)	0.102 (4)
C15	0.6394 (12)	0.0059 (3)	0.6488 (6)	0.090 (3)
C16	0.5828 (11)	0.0412 (3)	0.6668 (5)	0.079 (3)
N2	0.5319 (8)	0.1328 (3)	0.5391 (4)	0.071 (2)
C22	0.5675 (10)	0.0989 (3)	0.5071 (4)	0.071 (3)
C23	0.5787 (14)	0.0992 (5)	0.4344 (7)	0.106 (4)
C24	0.5576 (18)	0.1317 (6)	0.3953 (7)	0.132 (6)
C25	0.5233 (15)	0.1641 (5)	0.4274 (6)	0.123 (5)
C26	0.5131 (12)	0.1652 (3)	0.5002 (5)	0.086 (3)
N3	0.6941 (8)	0.1483 (3)	0.6881 (4)	0.074 (2)
C32	0.6884 (12)	0.1864 (3)	0.7055 (5)	0.077 (3)
C33	0.8186 (15)	0.2043 (4)	0.7387 (6)	0.105 (4)
C34	0.9538 (17)	0.1861 (6)	0.7537 (8)	0.124 (5)
C35	0.9602 (14)	0.1489 (6)	0.7359 (6)	0.113 (5)
C36	0.8276 (13)	0.1303 (4)	0.7020 (6)	0.096 (4)
N4	0.4310 (9)	0.1809 (2)	0.6553 (4)	0.072 (2)
C42	0.5335 (12)	0.2043 (3)	0.6886 (5)	0.075 (3)
C43	0.4986 (16)	0.2423 (4)	0.7066 (7)	0.101 (4)
C44	0.348 (2)	0.2535 (4)	0.6889 (8)	0.120 (5)
C45	0.2415 (15)	0.2293 (4)	0.6533 (7)	0.102 (4)
C46	0.2824 (11)	0.1921 (3)	0.6346 (5)	0.076 (3)
N5	0.2535 (8)	0.1264 (2)	0.5955 (4)	0.068 (2)
C52	0.1880 (11)	0.1620 (3)	0.5963 (5)	0.075 (3)
C53	0.0419 (13)	0.1701 (4)	0.5609 (6)	0.100 (4)
C54	−0.0374 (15)	0.1404 (6)	0.5260 (8)	0.131 (6)
C55	0.0275 (15)	0.1039 (5)	0.5251 (7)	0.112 (4)
C56	0.1753 (11)	0.0970 (4)	0.5607 (5)	0.081 (3)
N6	0.4110 (8)	0.1129 (2)	0.7400 (4)	0.062 (2)
C62	0.3163 (12)	0.0839 (3)	0.7457 (5)	0.074 (3)
C63	0.2415 (10)	0.0774 (3)	0.8026 (4)	0.067 (2)
C64	0.2617 (10)	0.1025 (3)	0.8606 (4)	0.060 (2)
C65	0.3665 (10)	0.1320 (3)	0.8573 (5)	0.072 (3)
C66	0.4416 (11)	0.1367 (3)	0.7972 (5)	0.074 (3)
C64′	0.1698 (10)	0.0991 (3)	0.9194 (4)	0.061 (2)
C65′	0.0332 (11)	0.0773 (3)	0.9125 (5)	0.081 (3)
C66′	−0.0528 (11)	0.0753 (3)	0.9686 (5)	0.081 (3)
N6′	−0.0156 (8)	0.0937 (2)	1.0301 (4)	0.061 (2)
C63′	0.2069 (10)	0.1180 (3)	0.9825 (5)	0.073 (3)
C62′	0.1129 (11)	0.1148 (3)	1.0368 (5)	0.072 (3)
Ru2	−0.15333 (7)	0.09012 (2)	1.10932 (3)	0.0590 (2)
N7	−0.3547 (9)	0.0983 (3)	1.0313 (4)	0.083 (2)
N8	−0.2981 (9)	0.0866 (2)	1.1926 (4)	0.083 (2)
N9	0.0439 (8)	0.0846 (2)	1.1890 (4)	0.080 (2)
N10	−0.1631 (8)	0.0284 (2)	1.0995 (4)	0.075 (2)
N11	−0.1425 (9)	0.1504 (2)	1.1235 (4)	0.083 (2)
P1	−0.0981 (3)	0.32268 (10)	0.6890 (2)	0.0891 (9)
F11	0.0772 (8)	0.3273 (3)	0.7203 (5)	0.158 (3)
F12	−0.2715 (8)	0.3189 (2)	0.6592 (5)	0.150 (3)
F13	−0.0700 (10)	0.2822 (3)	0.6591 (5)	0.158 (3)
F14	−0.1289 (10)	0.3043 (3)	0.7619 (4)	0.141 (3)
F15	−0.0658 (10)	0.3415 (3)	0.6183 (5)	0.172 (4)
F16	−0.1307 (11)	0.3641 (3)	0.7176 (7)	0.186 (4)
P2	0.3947 (3)	0.48600 (9)	0.84619 (14)	0.0791 (7)
F21	0.2453 (8)	0.5059 (3)	0.8702 (4)	0.138 (3)
F22	0.4708 (8)	0.5275 (2)	0.8430 (4)	0.108 (2)
F23	0.5414 (7)	0.4658 (2)	0.8233 (4)	0.115 (2)
F24	0.4670 (9)	0.4813 (3)	0.9264 (3)	0.133 (3)
F25	0.3236 (9)	0.4901 (2)	0.7647 (3)	0.129 (3)
F26	0.3142 (9)	0.4448 (2)	0.8483 (4)	0.127 (2)
P3	0.2432 (8)	0.2837 (2)	0.4482 (2)	0.160 (2)
F31	0.194 (2)	0.2437 (4)	0.4734 (7)	0.311 (10)
F32	0.1203 (16)	0.2848 (4)	0.3828 (5)	0.223 (6)
F33	0.296 (2)	0.3239 (5)	0.4310 (11)	0.313 (10)
F34	0.3734 (18)	0.2839 (5)	0.5138 (6)	0.273 (8)
F35	0.3551 (19)	0.2645 (5)	0.4026 (6)	0.269 (8)
F36	0.1377 (18)	0.3050 (5)	0.4968 (8)	0.276 (8)
P4	0.3632 (3)	0.00630 (9)	0.12000 (15)	0.0785 (7)
F41†	0.1920 (13)	0.0124 (4)	0.0855 (12)	0.167 (6)
F42†	0.3339 (19)	0.0375 (7)	0.1741 (12)	0.223 (9)
F43†	0.430 (2)	0.0376 (6)	0.0761 (10)	0.195 (7)
F44†	0.312 (2)	−0.0310 (6)	0.1557 (9)	0.184 (7)
F45†	0.5282 (14)	0.0003 (4)	0.1583 (11)	0.157 (6)
F46†	0.3832 (17)	−0.0212 (5)	0.0568 (8)	0.158 (5)
F41′‡	0.356 (3)	0.0511 (8)	0.1166 (17)	0.096 (7)
F42′‡	0.234 (3)	0.0009 (10)	0.1597 (17)	0.117 (9)
F43′‡	0.510 (4)	0.0077 (12)	0.086 (2)	0.149 (11)
F44′‡	0.454 (4)	0.0085 (11)	0.1876 (18)	0.128 (11)
F45′‡	0.371 (3)	−0.0357 (9)	0.106 (2)	0.110 (8)
F46′‡	0.254 (4)	0.0073 (10)	0.0512 (17)	0.123 (10)
N1*A*§	−0.094 (4)	0.1404 (10)	0.2938 (19)	0.154 (13)
N1*B*§	−0.038 (4)	0.1546 (11)	0.2812 (17)	0.143 (11)
C1*AB*	−0.060 (7)	0.1776 (17)	0.324 (3)	0.44 (3)
C1*A*§	0.119 (5)	0.1804 (12)	0.350 (2)	0.187 (15)
C2*B*§	−0.113 (4)	0.2051 (10)	0.3731 (18)	0.137 (10)

† Site occupancy = 0.70. ‡ Site occupancy = 0.30. § Site occupancy = 0.50.

Table 2. *Selected geometric parameters (Å, °)*

Ru1—N4	1.949 (9)	N6′—Ru2	2.052 (7)
Ru1—N2	2.044 (7)	Ru2—N11	2.089 (8)
Ru1—N3	2.073 (8)	Ru2—N10	2.129 (8)
Ru1—N5	2.078 (7)	Ru2—N9	2.140 (7)
Ru1—N1	2.092 (8)	Ru2—N8	2.157 (8)
Ru1—N6	2.112 (7)	Ru2—N7	2.158 (7)
N4—Ru1—N2	96.5 (3)	N6′—Ru2—N11	90.8 (3)
N4—Ru1—N3	78.9 (3)	N6′—Ru2—N10	90.9 (3)
N2—Ru1—N3	94.7 (3)	N11—Ru2—N10	177.6 (3)
N4—Ru1—N5	80.0 (3)	N6′—Ru2—N9	91.4 (3)
N2—Ru1—N5	85.5 (3)	N11—Ru2—N9	88.8 (3)
N3—Ru1—N5	158.7 (4)	N10—Ru2—N9	89.6 (3)
N4—Ru1—N1	173.8 (3)	N6′—Ru2—N8	179.8 (3)
N2—Ru1—N1	78.5 (3)	N11—Ru2—N8	89.0 (3)
N3—Ru1—N1	97.9 (3)	N10—Ru2—N8	89.3 (3)
N5—Ru1—N1	103.0 (3)	N9—Ru2—N8	88.6 (3)
N4—Ru1—N6	89.1 (3)	N6′—Ru2—N7	89.8 (3)
N2—Ru1—N6	171.1 (3)	N11—Ru2—N7	88.7 (3)
N3—Ru1—N6	93.1 (3)	N10—Ru2—N7	92.9 (3)
N5—Ru1—N6	88.7 (3)	N9—Ru2—N7	177.3 (3)
N1—Ru1—N6	96.4 (3)	N8—Ru2—N7	90.2 (3)

The original data set, collected with Mo $K\alpha$ radiation, resulted in too few observed reflections to complete the structure refinement (*SHELX*76; Sheldrick, 1976). A second data set, which was collected with Cu $K\alpha$ radiation, contained enough observed reflections to completely refine the structure (*SHELXL*93; Sheldrick, 1993) and resulted in a lower R value even though a large absorption correction had to be applied to the data. All non-H atoms were refined anisotropically, except for the set of F atoms with an occupancy factor of 0.3 and the atoms of the disordered acetonitrile molecule. A common isotropic U value was refined for all the bipyridine and terpyridine H atoms and a second common U value was refined for the ammine H atoms. The disordered acetonitrile molecule was refined using a model with two positions for the N atom and the methyl group, and a single atom representing the middle C atom. Weighted R factors, wR and all goodness-of-fit values, S, are based on F^2, while conventional R factors, R, are based on F, with F set to zero for negative F^2. Eight reflections were excluded from the refinement because $F_o^2 << F_c^2$. The observation criterion of $F^2 > 2\sigma(F^2)$ is used only for calculating $R_{\rm obs}$, *etc.*, and is not relevant to the choice of reflections for refinement. R factors based on F^2 are statistically about twice as large as those based on F and R factors based on all data will be even larger.

Data collection: *CAD*-4 *Operations Manual* (Enraf–Nonius, 1976). Cell refinement: *CAD*-4 *Operations Manual.* Data reduction: *KAPPA CRYSNET* (Berman, Bernstein, Bernstein, Koetzle & Williams, 1976). Program(s) used to solve structure: *SHELX*76. Program(s) used to refine structure: *SHELXL*93. Molecular graphics: *ORTEP*III (Burnett & Johnson, 1996).

Part of this work was performed at the Brookhaven National Laboratory under contract DE-AC02-76CH00016 with the US Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences. DJS would like to thank Baruch College for release time. Financial support from Consejo Nacional de Investigaciones Cientificas y Técnicas de la Republica Argentina (CONICET) and from Universidad Nacional de Tucumán (UNT, Argentina) is gratefully acknowledged. FF thanks CONICET for a Graduate Fellowship. NEK is a Member of the Research Career of CONICET.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1275). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Berman, H. M., Bernstein, F. C., Bernstein, H. J., Koetzle, T. F. & Williams, G. J. B. (1976). *CRYSNET Manual.* Informal Report BNL 21714. Brookhaven National Laboratory, New York, USA.

Binstead, R. A. & Meyer, T. J. (1987). *J. Am. Chem. Soc.* **109**, 3287–3297.

Burnett, M. N. & Johnson, C. K. (1996). *ORTEP*III. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.

Collin, J.-P., Guillerez, S., Sauvage, J.-P., Barigelletti, F., De Cola, L., Flamigni, L. & Balzani, V. (1991). *Inorg. Chem.* **30**, 4230–4238.

Constable, E. C. (1986). *Adv. Inorg. Chem. Radiochem.* **30**, 69–121, and references therein.

Creutz, C. (1983). *Prog. Inorg. Chem.* **30**, 1–73.

Enraf–Nonius (1976). *CAD*-4 *Operations Manual.* Enraf–Nonius, Delft, The Netherlands.

Fagalde, F. & Katz, N. E. (1993). *J. Chem. Soc. Dalton Trans.* pp. 571–575.

Fagalde, F. & Katz, N. E. (1995). *Polyhedron*, **14**, 1213–1220.

Fürholz, U., Joss, S., Bürgi, H. B. & Ludi, A. (1985). *Inorg. Chem.* **24**, 943–948.

Gress, M. E., Creutz, C. & Quicksall, C. O. (1981). *Inorg. Chem.* **20**, 1522–1528.

Grover, N., Gupta, N., Singh, P. & Thorp, H. H. (1992). *Inorg. Chem.* **31**, 2014–2020.

Hecker, C. R., Fanwick, P. E. & McMillin, D. R. (1991). *Inorg. Chem.* **30**, 659–666.

Hecker, C. R., Gushurst, A. K. I. & McMillin, D. R. (1991). *Inorg. Chem.* **30**, 538–541.

Leising, R. A., Kubow, S. A., Churchill, M. R., Buttrey, L. A., Ziller, J. W. & Takeuchi, K. J. (1990). *Inorg. Chem.* **29**, 1306–1312.

Meyer, T. J. (1978). *Acc. Chem. Res.* **11**, 94–100.

Moyer, B. A., Thompson, M. S. & Meyer, T. J. (1980). *J. Am. Chem. Soc.* **102**, 2310–2312.

Petersen, J. D., Morgan, L. W., Hsu, I., Billadeau, M. A. & Ronco, S. E. (1991). *Coord. Chem. Rev.* **111**, 319–324.

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

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Thompson, M. S. & Meyer, T. J. (1982). *J. Am. Chem. Soc.* **104**, 4106–4115.

Wishart, J. F., Bino, A. & Taube, H. (1986). *Inorg. Chem.* **25**, 3318–3321.

Woitellier, S., Launay, J. P. & Joachim, C. (1989). *Chem. Phys.* **131**, 481–488.

Acta Cryst. (1996). C**52**, 3016-3018

A 1:2 Adduct of Tetrakis(μ-thiobenzoato-*O*,*S*)dimolybdenum(II)(*Mo*—*Mo*) with Triphenylphosphine Oxide, $[Mo_2(C_7H_5OS)_4].2[(C_6H_5)_3OP]$

Marina Cindrić, Višnja Vrdoljak, Dubravka Matković-Čalogović and Boris Kamenar

Laboratory of General and Inorganic Chemistry, Faculty of Science, University of Zagreb, Ul. kralja Zvonimira 8, 10000 Zagreb, Croatia. E-mail: dmatkovic@olimp.irb.hr

(*Received 3 July 1996; accepted 1 August 1996*)

Abstract

The reaction of tetrakis(μ-thiobenzoato-*O*,*S*)dimolybdenum(II)(*Mo*—*Mo*) and triphenylphosphine oxide in a 1:2 stoichiometric ratio yields the title adduct. The dinuclear complex molecule, which has a quadruple Mo$\equiv$Mo bond bridged by four thiobenzoato ligands, is located on a centre of symmetry. This is the first structural example in which two quadruply bonded Mo atoms [2.152 (1) Å] are coordinated by both O and S

Acta Crystallographica Section C
ISSN 0108-2701 © 1996