SHORT-FORMAT PAPERS

Contributions intended for publication under this heading should follow the format given in the Checklist for Authors [*Acta Cryst.* (1985). C**41**, 1–4].

Acta Cryst. (1993). C**49**, 1117–1120

Structures of *ortho*-Metalated [2-(*p*-Tolyl)pyridine]iridium(III) Complexes

By Fred O. Garces, Kenneth Dedeian, Nancy L. Keder* and Richard J. Watts*

Department of Chemistry, University of California, Santa Babara, CA 93106, *USA*

(*Received* 2 *August* 1992; *accepted* 25 *January* 1993)

Abstract. Di-μ-chloro-tetrakis[2-(p-tolyl-κC^2)pyridine-κN]diiridium(III) toluene solvate, (I), $[Ir_2(Cl_2)(C_{12}H_{10}N)_4]\cdot 0.5C_7H_8$, $M_r = 1174.3$, tetragonal, $I4_1cd$, $a = 16.90\,(2)$, $c = 33.31\,(3)$ Å, $V = 9513.7$ Å^3, $Z = 8$, $D_x = 1.64$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å (graphite monochromator), $\mu = 57.18$ cm^{-1}, $F(000) = 4552$, $T = 296$ K, $R = 0.044$ for 1420 reflections with $I > 3\sigma(I)$. Tris[2-(p-tolyl-κC^2)pyridine-κN]iridium(III), (II), $[Ir(C_{12}H_{10}N)_3]$, $M_r = 696.87$, trigonal (hexagonal axes), $R\bar{3}$, $a = 15.0144\,(7)$, $c = 25.829\,(1)$ Å, $V = 5042.6$ Å^3, $Z = 6$, $D_x = 1.38$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å (graphite monochromator), $\mu = 39.82$ cm^{-1}, $F(000) = 2064$, $T = 296$ K, $R = 0.055$ for 2751 reflections with $I > 3\sigma(I)$. This report describes the crystallographic results for two iridium–carbon σ-bonded *ortho*-metalated complexes, the dichloro-bridged dimer, $[Ir(ptpy)_2Cl]_2$ (I), and the *facial*-tris mononuclear complex, $Ir(ptpy)_3$ (II), where ptpy is the deprotonated 2-(p-tolyl)pyridine, $C_{12}H_{10}N$. Complex (I) has crystallographic twofold symmetry (Cl atoms on the twofold axis) and (II) has crystallographic threefold symmetry (Ir atom on the threefold axis). These molecules have been synthesized and studied for their utilization in outer-sphere electron-transfer processes.

Experimental. Synthetic procedures for preparation of (I) and (II) have been described in prior publications (Sprouse, King, Spellane & Watts, 1984; King, Spellane & Watts, 1985; Garces, King & Watts, 1988; Dedeian, Djurovich, Garces, Carlson & Watts, 1991). Complex (I): crystals were obtained by vapor exchange of a dichloromethane solution with toluene/hexane (2:1). A gold pyramidal crystal (*ca* 0.18 × 0.39 × 0.37 mm) was epoxied to a glass fiber and diffraction data were collected on a Huber (Crystal-Logic automated) four-circle diffractometer in the $\theta/2\theta$ scan mode to a maximum 2θ of 50° at a scan rate of 4.5° min^{-1}. The lattice parameters were determined from 32 reflections in the range $10.0 < 2\theta < 25.7°$. Three standard reflections measured after every 97 reflections indicated no appreciable intensity change. The intensities were corrected for Lorentz and polarization effects and an empirical absorption correction (North, Phillips & Mathews, 1968) was applied ($T_{\max} = 1.0$, $T_{\min} = 0.388$); maximum $\sin\theta/\lambda = 0.595$ Å^{-1}; $0 \le h \le 12$, $0 \le k \le 18$, $0 \le l \le 35$. A total of 3212 reflections were measured, of which 1737 were unique ($R_{\rm int} = 4.4\%$) and 317 unobserved. The Ir and Cl atoms were located by direct methods using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). The two half-occupancy Cl atoms are located on the twofold axis at $x = 1/2$, $y = 0$; the z coordinate of Ir was fixed to define the origin of the unit cell. C and N atoms were located by successive cycles of least-squares refinement and difference Fourier syntheses. Phenyl H-atom positions were calculated (C—H = 0.95 Å) and methyl H-atom positions were located in the difference maps or calculated; H atoms were included as fixed contributors with thermal parameters of 3.0 Å^2. A difference map revealed a toluene solvate disordered about the twofold axis at $x = y = 1/2$. It was refined as a rigid group with idealized geometry (Strouse, 1970) and individual isotropic thermal parameters; H atoms were not included. In the final refinement the x and y coordinates of the Ir, the z coordinates of the Cl atoms, and the x, y, z coordinates for all C and N atoms of the ligands were refined. Anisotropic thermal parameters were refined for the Ir, Cl and methyl C atoms; the thermal parameters of all other non-H atoms were refined isotropically. The final cycle afforded the convergence of R to 4.4% and wR to 6.0% for 142 refined parameters; $S = 2.16$; $(\Delta/\sigma)_{\max} = 0.056$; $\Delta\rho_{\max,\min} = 1.01$, -2.07 e Å^{-3}. The space group

---

* Authors to whom correspondence should be addressed.

0108-2701/93/061117-04$06.00

Table 1. *Atomic coordinates and isotropic thermal parameters* ($Å^2 \times 10^3$) *for* $[Ir(ptpy)_2Cl]_2$ (I) *and* $Ir(ptpy)_3$ (II) *with e.s.d.'s in parentheses*

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

	x	y	z	U
Compound (I)				
Ir(1)	0.50865 (3)	0.11124 (4)	0.20224	54 (1)*
Cl(1)	0.5000	0.0000	0.2547 (5)	64 (10)*
Cl(2)	0.5000	0.0000	0.1530 (5)	68 (10)*
C(103)	0.4297 (17)	0.3222 (23)	0.0792 (10)	160 (31)*
C(203)	0.6183 (17)	0.3187 (16)	0.3224 (8)	103 (19)*
C(1)	0.5270 (13)	0.1907 (12)	0.1577 (6)	56 (5)
C(2)	0.4716 (12)	0.2317 (13)	0.1369 (6)	72 (5)
C(3)	0.4918 (12)	0.2797 (15)	0.1022 (7)	71 (6)
C(4)	0.5703 (17)	0.2780 (15)	0.0919 (8)	95 (8)
C(5)	0.6253 (13)	0.2425 (13)	0.1132 (7)	80 (6)
C(6)	0.6074 (11)	0.1953 (11)	0.1469 (6)	62 (5)
C(7)	0.6625 (12)	0.1515 (13)	0.1703 (6)	73 (6)
C(8)	0.7488 (14)	0.1502 (14)	0.1651 (7)	90 (7)
C(9)	0.7898 (15)	0.1070 (16)	0.1932 (8)	98 (8)
C(10)	0.7610 (17)	0.0700 (17)	0.2246 (8)	103 (8)
C(11)	0.6787 (12)	0.0698 (13)	0.2288 (7)	77 (6)
N(1)	0.6324 (8)	0.1094 (9)	0.2006 (7)	65 (4)
C(21)	0.5036 (10)	0.1931 (13)	0.2462 (7)	58 (6)
C(22)	0.5661 (11)	0.2292 (11)	0.2682 (6)	61 (5)
C(23)	0.5536 (13)	0.2827 (13)	0.3004 (7)	78 (6)
C(24)	0.4694 (18)	0.3033 (16)	0.3103 (8)	90 (7)
C(25)	0.4125 (13)	0.2713 (14)	0.2886 (7)	87 (7)
C(26)	0.4251 (12)	0.2185 (12)	0.2576 (6)	69 (5)
C(27)	0.3632 (11)	0.1826 (11)	0.2324 (6)	66 (5)
C(28)	0.2798 (13)	0.1978 (13)	0.2369 (6)	78 (6)
C(29)	0.2286 (12)	0.1613 (13)	0.2129 (7)	77 (6)
C(30)	0.2544 (14)	0.1090 (15)	0.1825 (7)	82 (6)
C(31)	0.3354 (12)	0.0935 (12)	0.1797 (6)	70 (5)
N(2)	0.3865 (7)	0.1294 (10)	0.2049 (7)	67 (4)
Compound (II)				
Ir(12)	0.33333	0.66667	−0.09346 (2)	459 (1)*
C(10)	0.2184 (5)	0.5503 (4)	−0.0532 (2)	463 (45)*
C(11)	0.2258 (5)	0.4933 (5)	−0.0122 (3)	538 (54)*
C(12)	0.1405 (6)	0.4140 (5)	0.0115 (3)	601 (62)*
C(13)	0.0416 (6)	0.3885 (5)	−0.0056 (3)	610 (61)*
C(14)	0.0311 (5)	0.4419 (5)	−0.0444 (3)	576 (55)*
C(15)	0.1182 (4)	0.5226 (4)	−0.0694 (2)	498 (48)*
C(16)	0.1106 (5)	0.5830 (5)	−0.1130 (3)	529 (51)*
C(17)	0.0191 (5)	0.5745 (6)	−0.1324 (3)	679 (70)*
C(18)	0.0226 (7)	0.6350 (7)	−0.1719 (3)	760 (89)*
C(19)	0.1168 (7)	0.7058 (7)	−0.1928 (3)	748 (86)*
C(20)	0.2041 (6)	0.7122 (6)	−0.1726 (3)	674 (68)*
N(21)	0.2035 (5)	0.6528 (4)	−0.1342 (2)	548 (49)*
C(22)	0.1541 (7)	0.3571 (7)	0.0556 (4)	861 (94)*

* Calculated using equation for U_{eq} above.

Table 2. *Selected bond distances* (Å) *and angles* (°) *for* $[Ir(ptpy)_2Cl]_2$ (I) *and* $Ir(ptpy)_3$ (II) *with e.s.d.'s in parentheses*

Compound (I)			
Ir(1)—C(21)	2.02 (2)	C(9)—C(10)	1.31 (3)
Ir(1)—C(1)	2.03 (2)	C(10)—C(11)	1.40 (3)
Ir(1)—N(2)	2.09 (1)	C(11)—N(1)	1.39 (3)
Ir(1)—N(1)	2.09 (1)	C(21)—C(22)	1.42 (3)
Ir(1)—Cl(2)	2.50 (1)	C(21)—C(26)	1.44 (3)
Ir(1)—Cl(1)	2.57 (1)	C(22)—C(23)	1.42 (3)
C(1)—C(2)	1.35 (3)	C(23)—C(203)	1.45 (3)
C(1)—C(6)	1.41 (3)	C(23)—C(24)	1.50 (4)
C(2)—C(3)	1.45 (3)	C(24)—C(25)	1.32 (3)
C(3)—C(4)	1.37 (3)	C(25)—C(26)	1.38 (3)
C(3)—C(103)	1.49 (3)	C(26)—C(27)	1.47 (3)
C(4)—C(5)	1.31 (3)	C(27)—N(2)	1.34 (3)
C(5)—C(6)	1.41 (3)	C(27)—C(28)	1.44 (3)
C(6)—C(7)	1.42 (3)	C(28)—C(29)	1.33 (3)
C(7)—N(1)	1.34 (3)	C(29)—C(30)	1.41 (3)
C(7)—C(8)	1.47 (3)	C(30)—C(31)	1.40 (3)
C(8)—C(9)	1.37 (3)	C(31)—N(2)	1.35 (3)
C(1)—Ir(1)—N(2)	94.9 (8)	C(7)—N(1)—Ir(1)	113.2 (14)
C(1)—Ir(1)—C(21)	94.8 (6)	C(11)—N(1)—Ir(1)	123.4 (15)
C(1)—Ir(1)—N(1)	80.6 (8)	C(6)—C(1)—C(2)	120.6 (21)
C(1)—Ir(1)—Cl(2)	91.6 (7)	C(5)—C(6)—C(7)	126.1 (19)
C(1)—Ir(1)—Cl(1)	172.6 (6)	C(7)—C(6)—C(1)	117.7 (19)
N(2)—Ir(1)—C(21)	80.0 (7)	N(1)—C(7)—C(6)	116.1 (18)
N(2)—Ir(1)—N(1)	172.4 (6)	C(6)—C(7)—C(8)	126.5 (20)
N(2)—Ir(1)—Cl(2)	94.6 (5)	C(27)—N(2)—Ir(1)	114.7 (13)
N(2)—Ir(1)—Cl(1)	91.3 (5)	C(31)—N(2)—Ir(1)	122.8 (14)
C(21)—Ir(1)—N(1)	94.1 (7)	C(22)—C(21)—C(26)	114.8 (19)
C(21)—Ir(1)—Cl(2)	172.0 (6)	C(22)—C(21)—Ir(1)	129.6 (14)
C(21)—Ir(1)—Cl(1)	90.3 (7)	C(26)—C(21)—Ir(1)	115.7 (13)
N(1)—Ir(1)—Cl(2)	91.7 (5)	C(25)—C(26)—C(21)	122.0 (19)
N(1)—Ir(1)—Cl(1)	93.7 (5)	C(21)—C(26)—C(27)	112.4 (17)
Cl(2)—Ir(1)—Cl(1)	83.9 (2)	N(2)—C(27)—C(28)	118.6 (17)
Ir(1)—Cl(1)—Ir(1)*	94.3 (5)	C(28)—C(27)—C(26)	124.2 (18)
Ir(1)—Cl(2)—Ir(1)*	97.9 (6)	N(2)—C(27)—C(26)	117.2 (17)
C(7)—N(1)—C(11)	123.4 (16)		
Compound (II)			
Ir(12)—C(10)	2.024 (6)	C(14)—C(15)	1.418 (9)
Ir(12)—N(21)	2.132 (5)	C(15)—C(16)	1.487 (9)
C(10)—C(11)	1.401 (9)	C(16)—N(21)	1.371 (9)
C(10)—C(15)	1.409 (8)	C(16)—C(17)	1.407 (9)
C(11)—C(12)	1.382 (9)	C(17)—C(18)	1.350 (12)
C(12)—C(13)	1.407 (11)	C(18)—C(19)	1.384 (12)
C(12)—C(22)	1.496 (11)	C(19)—C(20)	1.369 (11)
C(13)—C(14)	1.341 (10)	C(20)—N(21)	1.331 (9)
C(10)—Ir(12)—C(10)	96.0 (2)	C(10)—C(15)—C(14)	120.6 (6)
N(21)—Ir(12)—N(21)	97.8 (2)	C(10)—C(15)—C(16)	116.2 (5)
C(10)—Ir(12)—N(21)	80.0 (2)	C(14)—C(15)—C(16)	123.2 (6)
C(10)—Ir(12)—N(21)†	86.4 (2)	N(21)—C(16)—C(17)	120.1 (6)
C(10)—Ir(12)—N(21)†	175.5 (2)	N(21)—C(16)—C(15)	114.1 (5)
C(11)—C(10)—C(15)	116.3 (6)	C(17)—C(16)—C(15)	125.7 (6)
C(11)—C(10)—Ir(12)	128.5 (5)	C(18)—C(17)—C(16)	120.0 (8)
C(15)—C(10)—Ir(12)	115.2 (4)	C(17)—C(18)—C(19)	119.5 (7)
C(12)—C(11)—C(10)	122.6 (6)	C(20)—C(19)—C(18)	118.8 (7)
C(11)—C(12)—C(13)	119.5 (6)	N(21)—C(20)—C(19)	123.4 (7)
C(11)—C(12)—C(22)	119.8 (7)	C(20)—N(21)—C(16)	118.2 (6)
C(13)—C(12)—C(22)	120.7 (7)	C(20)—N(21)—Ir(12)	127.0 (5)
C(14)—C(13)—C(12)	119.7 (6)	C(16)—N(21)—Ir(12)	114.2 (4)
C(13)—C(14)—C(15)	121.2 (6)		

* Atoms related by the twofold axis at $\frac{1}{2}$, 0, z.
† Atoms related by the threefold axis at $\frac{1}{3}$, $\frac{2}{3}$, z.

$I4_1cd$ is polar; the structural coordinates were inverted through 0, 1/4, 1/8 and the structure refined; convergence at a higher R factor confirmed the original choice of polarity. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The *UCLA Crystallographic Computing Package* (Strouse, 1985) was used throughout. Positional parameters and equivalent isotropic temperature factors for (I) are listed in Table 1;* selected bond distances and bond angles are summarized in Table 2; and the atomic labeling scheme for the $\Lambda\Lambda$ enantiomer of (I) is shown in Fig. 1. In this figure, the starred (*) atoms are generated by the twofold axis. Complex (II): crystals were obtained by vapor exchange of a 2-methyl THF [1% butylated hydroxytoluene (BHT) inhibited] solution with methanol. A yellow crystal (*ca* 0.31 × 0.40 × 0.29 mm) was wedged inside a glass capillary containing the mother liquor and the capillary sealed with epoxy. The data collection and analysis for this structure were analogous to (I) with the following exceptions: the lattice parameters were determined

---

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and complete bond distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55883 (35 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR1031]

from 44 reflections ($7.0 \leq 2\theta \leq 26.1°$); scan rate of 6.0° $\min^{-1}$; maximum 2θ of 60°; absorption correction ($T_{\max} = 1.0$, $T_{\min} = 0.593$); maximum $\sin\theta/\lambda = 0.704$ Å^{-1}; $-10 \leq h \leq 20$, $-9 \leq k \leq 20$, $0 \leq l \leq 36$; a total of 3617 reflections were measured, of which 3276 were unique ($R_{\rm int} = 3.4\%$) and 525 unobserved; and *SHELXS* (Sheldrick, 1985) was utilized to locate the Ir atom. The hexagonal unit cell accommodates six molecules lying on threefold axes. Anisotropic thermal parameters were allowed to refine for all non-H atoms. The final cycle converged to $R = 5.5\%$ and $wR = 7.2\%$, for 121 refined parameters; $S = 2.37$; $(\Delta/\sigma)_{\max} = 0.024$; $\Delta\rho_{\max,\min} = 0.91$, -1.42 e Å^{-3}. Positional parameters and equivalent isotropic temperature factors are listed in Table 1; selected bond distances and bond angles are given in Table 2; and the atomic labeling scheme for the Δ enantiomer of (II) is shown in Fig. 2. In this figure, the primed atoms and the double-primed atoms are generated by the threefold axis.

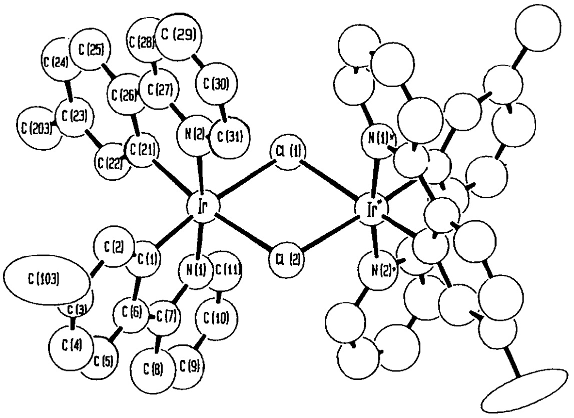

Fig. 1. Molecular structure of the $\Lambda\Lambda$ $[\mathrm{Ir(ptpy)_2Cl}]_2$ enantiomer; starred (*) atoms related by the twofold axis. *ORTEP*II (Johnson, 1976) drawing (50% probability ellipsoids) was modified using *PLOTMD* (Luo, Ammon & Gilliland, 1989). H atoms and the toluene solvate are omitted for clarity.

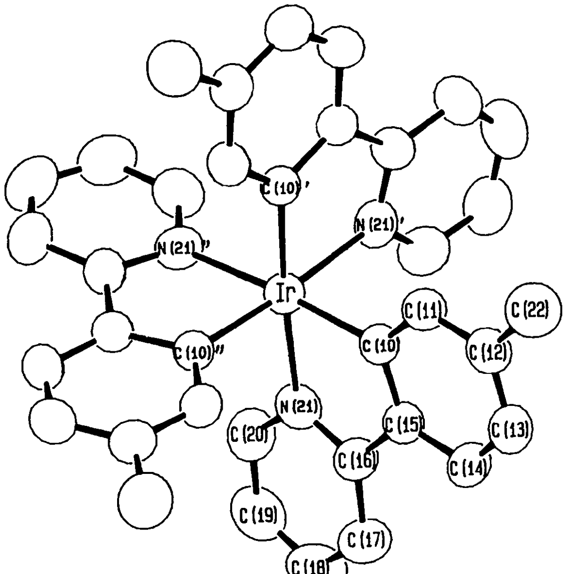

Fig. 2. Molecular structure of the Δ $[\mathrm{Ir(ptpy)_3}]$ enantiomer; primed and double-primed atoms are related by the threefold axis. *ORTEP*II (Johnson, 1976) drawing (50% probability ellipsoids) was modified using *PLOTMD* (Luo, Ammon & Gilliland, 1989). H atoms are omitted for clarity.

Related literature. *ortho*-Metalated complexes whose structures are reported in the literature include [Ir(2,2′-bipyridine-N,N')$_2$(2,2′-bipyridine-C^3,N')] (Wickramasinghe, Bird & Serpone, 1981; Spellane, Watts & Curtis, 1983), [Ir(H)(CO)(benzo[*h*]quinoline-C^{10},N')(PPh$_3$)$_2$]PF$_6$ (Neve, Mauro, Tiripicchio & Ugozzoli, 1989) and [Ru(bpy)$_2$(NO$_2$-2-phenylpyridine)]$^+$ (Reveco, Schmehl, Cherry, Fronczek & Selbin, 1985). Related iridium complexes which possess Ir—C bonds *trans* to Ir—Cl bonds include $[\mathrm{Ir\{C_3(C_6H_5)_3\}Cl(CO)\{P(CH_3)_3\}_2}]^+$ (Tuggle & Weaver, 1972) and $[\mathrm{Ir(CH_3)_2CO_2Cl_2}]^-$ (Bailey, Jones, Shaw & Singleton, 1967). Finally, the structure of [Rh(2-phenylpyridine)$_2$Cl]$_2$ has been determined (Attia, Kaska, Sprouse & Watts, 1984).

Financial support of this research was by the Office of Basic Energy Sciences, United States Department of Energy, Contract DE-FG03-88ER13842.

References

Attia, W. M., Kaska, W., Sprouse, S. & Watts, R. J. (1984). Unpublished results.

Bailey, N. A., Jones, C. J., Shaw, B. L. & Singleton, E. (1967). *J. Chem. Soc. Chem. Commun.* pp. 1051–1052.

Dedeian, K., Djurovich, P., Garces, F., Carlson, G. & Watts, R. J. (1991). *Inorg. Chem.* **30**, 1685–1687.

Garces, F. O., King, K. A. & Watts, R. J. (1988). *Inorg. Chem.* **27**, 3464–3471.

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

King, K. A., Spellane, P. J. & Watts, R. J. (1985). *J. Am. Chem. Soc.* **107**, 1431–1432.

Luo, J., Ammon, H. L. & Gilliland, G. L. (1989). *J. Appl. Cryst.* **22**, 186.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Neve, F., Mauro, G., Tiripicchio, A. & Ugozzoli, A. (1989). *Inorg. Chem.* **28**, 3084–3086.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Reveco, P., Schmehl, H., Cherry, W. R., Fronczek, F. R. & Selbin, J. (1985). *Inorg. Chem.* **24**, 4078–4082.

Sheldrick, G. M. (1985). *SHELXS86*. In *Crystallographic Computing* 3, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 175–189. Oxford Univ. Press.

Spellane, P.J., Watts, R. J. & Curtis, C. J. (1983). *Inorg. Chem.* **22**, 4060–4062.

SPROUSE, S. D., KING, K. A., SPELLANE, P. J. & WATTS, R. J. (1984). *J. Am. Chem. Soc.* **106**, 6647–6653.
STROUSE, C. (1985). *UCLA Crystallographic Computing Package.* Department of Chemistry and Biochemistry, Univ. of California, Los Angeles, USA.
STROUSE, C. E. (1970). *Acta Cryst.* **A26**, 604–608.
TUGGLE, R. M. & WEAVER, D. L. (1972). *Inorg. Chem.* **11**, 2237–2242.
WICKRAMASINGHE, W. A., BIRD, P. H. & SERPONE, N. (1981). *J. Chem. Soc. Chem. Commun.* pp. 1284–1286.

Acta Cryst. (1993). C**49**, 1120–1121

Structure of Bis[(bipyridyl)dicyanatocopper(II)](*Cu–Cu*)

BY M. KABEŠOVÁ, V. JORÍK AND M. DUNAJ-JURČO

Department of Inorganic Chemistry, Slovak Technical University, 81237 Bratislava, Czechoslovakia

(*Received* 20 *July* 1992; *accepted* 7 *December* 1992)

Abstract. $[Cu_2(NCO)_4(C_{10}H_8N_2)_2]$, $M_r = 607.5$, triclinic, $P\bar{1}$, $a = 6.62\,(1)$, $b = 9.99\,(1)$, $c = 10.40\,(1)$ Å, $\alpha = 118.4\,(1)$, $\beta = 95.3\,(1)$, $\gamma = 102.8\,(1)°$, $V = 574.1\,(19)$ Å^3, $Z = 1$, $D_m = 1.74$, $D_x = 1.757$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 1.98$ mm^{-1}, $F(000) = 306$, room temperature, $R = 0.0490$, $wR = 0.0471$ for 1652 reflections with $I \geq 2\sigma(I)$. Each Cu atom is involved in tetragonal pyramidal coordination and has an N_4Cu donor set. The N atoms of the cyanate and bipyridyl ligands define a square plane from which the central Cu atom is slightly displaced in the axial direction. An axial Cu—Cu bond (3.375 Å) links the $[Cu(NCO)_2(bpy)]$ units into centrosymmetric dimers which lie in parallel layers in the crystal structure. The occurrence of the Cu—Cu bond may explain why only one bipyridyl ligand can be accommodated in the coordination sphere of each Cu^{II} ion.

Experimental. Blue prism-shaped crystals of poor quality; density measured by flotation, dimensions 0.45 × 0.1 × 0.065 mm. A Syntex $P2_1$ four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation was used for data collection. 20 reflections with $4.91 \leq \theta \leq 12.72°$ were used for determination of the lattice parameters. Extinction was ignored. Intensity measurements from ω–2θ scans were made for $0 \leq 2\theta \leq 55°$; h −8 to 8, k −7 to 7, l 0 to 14. Two standard reflections monitored every 98 measurements; intensity fluctuations did not exceed 1% during the course of the experiment; corrections for decomposition were therefore not applied. 1652 independent reflections with $I \geq 2\sigma(I)$ were collected (925 unobserved reflections). 196 parameters were refined. The position of the Cu atom was obtained from the Patterson function, positions of the other atoms (including H atoms) from Fourier syntheses. Anisotropic full-matrix refinement on F for non-H atoms. H atoms were assigned a fixed isotropic displacement parameter $U = 0.1$ Å^2 and only their fractional coordinates were refined. $R = 0.0490$, $wR = 0.0471$, $w = k/[\sigma^2(F_o) + g(F_o)^2]$, $k = 1.0464$, $g = 0.001010$, $\Delta\rho_{max} = 0.52$, $\Delta\rho_{min} = -0.31$ e Å^{-3}. $(\Delta/\sigma)_{max}$ in the final least-squares cycle was 0.120 for non-H atoms and 0.350 for H atoms. Calculations were performed with *SHELX*76 (Sheldrick, 1976); scattering factors were obtained from *International Tables for X-ray Crystallography* (1974, Vol. IV). Positional and equivalent isotropic thermal parameters for non-H atoms are in Table 1.* Table 2 gives selected interatomic distances and bond angles.

Related literature. In the crystal structure of $[Cu_2(NCO)_4(bpy)_2]$ (Fig. 1) the Cu atom has tetragonal pyramidal coordination. N atoms from the bipyridyl and cyanate ligands form a slightly distorted square plane and there is another Cu atom, Cu′, in the axial position, at a distance of 3.375 (6) Å. The coordination of bipyridyl in the equatorial plane of a Cu^{II} coordination polyhedron is uncommon. The cyanate ligands are terminally bound and virtually linear. The copper coordination closely resembles that observed in $[Cu_2(NCO)_4(phen)_2]$ (phen = 1,10-phenanthroline) (Jin, Kabešová & Kožíšek, 1991) and is in agreement with the maximum found *ca* 16000 cm^{-1} in the absorption spectrum of the complex.

---

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55843 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU1023]

0108-2701/93/061120-02$06.00