Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å²)

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

	x	y	z	U_{eq}
Cl	0.05483 (10)	0.21486 (12)	0.39358 (9)	0.0502 (6)
C1	−0.1741 (4)	0.0615 (6)	0.4496 (4)	0.046 (2)
O2	0.0411 (2)	0.1427 (3)	0.6493 (2)	0.040 (1)
C3	−0.0227 (3)	0.2079 (4)	0.7048 (3)	0.033 (2)
C4	−0.1137 (4)	0.1393 (5)	0.7339 (4)	0.045 (2)
C5	−0.1777 (4)	0.2070 (6)	0.7936 (4)	0.054 (3)
C6	−0.1544 (5)	0.3464 (6)	0.8288 (4)	0.061 (3)
C7	−0.0666 (4)	0.4169 (5)	0.8033 (4)	0.055 (3)
C8	0.0003 (3)	0.3506 (4)	0.7398 (3)	0.038 (2)
C9	0.0897 (4)	0.4309 (5)	0.7141 (3)	0.043 (2)
N10	0.1549 (3)	0.3824 (4)	0.6564 (3)	0.043 (2)
C11	0.2456 (4)	0.4644 (5)	0.6277 (4)	0.051 (3)
C12	0.1998 (6)	0.5460 (7)	0.5213 (6)	0.068 (4)
C13	0.3389 (3)	0.3565 (5)	0.6216 (3)	0.045 (2)
O14	0.3359 (3)	0.2328 (3)	0.6401 (3)	0.059 (2)
O15	0.4243 (3)	0.4211 (3)	0.5929 (3)	0.058 (2)
C16	0.5215 (5)	0.3341 (7)	0.5895 (5)	0.065 (3)

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

Sn—Cl	2.599 (1)	C7—C8	1.418 (5)
Sn—O2	2.244 (3)	C8—C9	1.423 (6)
Sn—C1	2.111 (4)	C9—N10	1.286 (5)
O2—C3	1.318 (4)	N10—C11	1.461 (6)
C3—C4	1.403 (6)	C11—C12	1.508 (8)
C3—C8	1.415 (5)	C11—C13	1.533 (7)
C4—C5	1.367 (6)	C13—O14	1.187 (5)
C5—C6	1.386 (7)	C13—O15	1.327 (5)
C6—C7	1.359 (7)	O15—C16	1.441 (6)
O2—N10	2.628 (4)	O2···H10	1.98 (4)
N10—H10	0.81 (4)		
Cl—Sn—C1	90.2 (2)	C3—C8—C9	122.1 (3)
Cl—Sn—O2	86.1 (1)	C7—C8—C9	118.3 (4)
C1—Sn—O2	93.9 (1)	C8—C9—N10	123.7 (4)
Sn—O2—C3	133.2 (2)	C9—N10—C11	124.3 (4)
O2—C3—C4	122.1 (3)	N10—C11—C12	111.1 (4)
O2—C3—C8	120.6 (3)	N10—C11—C13	105.9 (3)
C4—C3—C8	117.2 (4)	C12—C11—C13	113.2 (4)
C3—C4—C5	121.7 (4)	C11—C13—O14	125.2 (4)
C4—C5—C6	121.1 (5)	C11—C13—O15	110.3 (4)
C5—C6—C7	119.4 (5)	O14—C13—O15	124.4 (4)
C6—C7—C8	121.0 (5)	C13—O15—C16	116.7 (4)
C3—C8—C7	119.6 (4)	O2···H10—N10	137 (4)

Cell dimensions were determined from reflections measured at four positions, $\pm 2\theta$ and high and low χ. Data were corrected for background, Lorentz and polarization effects, and for absorption. The structure was determined using *SHELXS*86 (Sheldrick, 1986) and H atoms were located from a difference electron density map. Non-H atoms were refined anisotropically and H atoms isotropically using a modification of *ORFLS* (Busing, Martin & Levy, 1962).

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and bond distances and angles including H-atom geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71378 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1077]

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References

Bullock, J. L., Ladd, M. F. C., Povey, D. C. & Tajmir-Riahi, H. A. (1979). *Acta Cryst.* B**35**, 2013–2020.

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee, USA.

Kamwaya, M. E. & Khoo, L. E. (1985). *Acta Cryst.* C**41**, 1027–1029.

Lee, F. L., Gabe, E. J., Khoo, L. E., Eng, G. & Smith, F. E. (1990). *Polyhedron*, **9**, 653–657.

Randaccio, L. (1973). *J. Organomet. Chem.* **55**, C58–C60.

Sheldrick, G. M. (1986). *SHELXS*86. *Program for the Solution of Crystal Structures*. Univ. of Göttingen, Germany.

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Structure of Bis(2,2′-bipyridyl)diisocyanatonickel(II)

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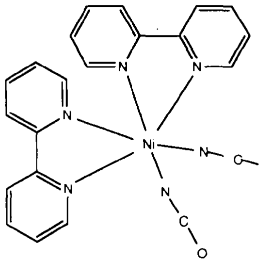
Abstract

Blue–grey crystals of [$Ni(bipy)_2(NCO)_2$] (where bipy is 2,2′-bipyridine) were prepared and its structure determined. There are discrete molecules with symmetry 2. The Ni^{II} ion is octahedrally coordinated by six N atoms, with some slight distortion towards a trigonal prism.

Comment

Recently, our group has studied complexes of copper(II) and nickel(II) ions with tridentate ligands, [$M(L_{III})(X)_2$] (L_{III} = tridentate ligand; X = halide or pseudohalide), as precursors to polynuclear species (Cortés, Arriortua, Rojo, Solans & Beltrán, 1986; Cortés *et al.*, 1988; Arriortua *et al.*, 1988; Via, Arriortua, Rojo, Mesa & García, 1989). Knowledge of the crystal structures of these precursors is very useful in developing new synthetic routes for desired polynuclear compounds. This crystal structure determination aims to evaluate the effect of replacing a tridentate ligand with two bidentate ones. The bidentate ligand, 2,2′-bipyridine, was chosen because comparatively few nickel(II)–pseudohalide complexes have been crystallographically characterized.

The complex (I) was prepared by mixing an aqueous solution of Ni(bipy)$_2$Cl$_2$ [previously prepared by reaction of nickel(II) chloride and bipy ligand in 1:2 proportion] with a saturated aqueous solution of potassium cyanate. Slow evaporation at room temperature gave well formed prismatic crystals. Elemental analysis and atomic absorption results agree well with the stoichiometry: [Ni(C$_{10}$H$_8$N$_2$)$_2$(NCO)$_2$].



(I)

The distortion of the octahedral geometry has been evaluated by the method of Muetterties & Guggenberger (1974), giving $\Delta = 0.11$, close to that for an octahedron ($\Delta = 0$) (Table 3 gives the corresponding dihedral angles and the expression employed to calculate Δ). The *cis* configuration of the cyanate groups would allow the compound to act as a ligand, by coordinating to a second metal. The Ni—N—C angle [172.8 (5)°] and the N3—C11 bond distance [1.131 (9) Å] are consistent with the existence of a C≡N triple bond (Nardelli, 1983). The bond lengths and angles are comparable with those found previously in Ni$^{\rm II}$–bipyridine complexes (Tedenac & Philippot, 1974; Healy, Patrick & White, 1984). In the bipy ligand the maximum deviations from planarity are at C3 [−0.156 (7) Å] and C7 [0.166 (6) Å]; its great rigidity forces the angle N1—Ni—N2 to be 77.3 (2)°, significantly less than 90°.

Cyanate groups exhibit absorptions in the infrared 2000–2200 cm^{-1} region which have been used to distinguish between the different coordination modes of this ligand (ionic, monodentate or bridging) (Lever, Mantovani & Ramaswamy, 1971). In this compound a single absorption at 2200 cm^{-1} is observed, in agreement with monodentate coordination of the cyanate ligand through its N atom.

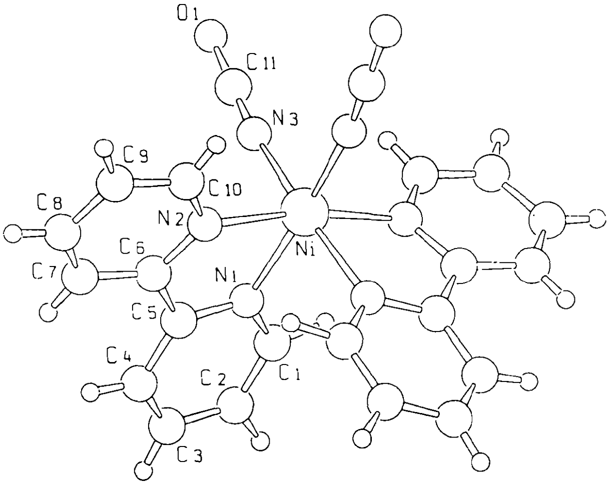


Fig. 1. View of [Ni(bipy)$_2$(NCO)$_2$] showing the labelling of the non-H atoms.

Experimental

Crystal data

[Ni(C$_{10}$H$_8$N$_2$)$_2$(NCO)$_2$]
M_r = 454.71
Orthorhombic
Pbcn
a = 13.9571 (7) Å
b = 9.8457 (8) Å
c = 15.231 (2) Å
V = 2093.0 (3) Å^3
Z = 4
D_x = 1.443 Mg m^{-3}
D_m = 1.44 (3) Mg m^{-3}
Density measured by flotation in bromoform/acetone

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 8-14°
μ = 0.959 mm^{-1}
T = 298 K
Block
0.38 × 0.30 × 0.24 mm
Blue-grey

Data collection

Enraf-Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3519 measured reflections
3435 independent reflections
977 observed reflections [$I \geq 2.5\sigma(I)$]

$\theta_{\rm max}$ = 30°
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 19$
$l = 0 \rightarrow 21$
2 standard reflections intensity variation: 5.75%

Refinement

Refinement on F
R = 0.0395
wR = 0.0407
S = 1.53
977 reflections
165 parameters
Only coordinates of H atoms refined

$w = 1/(\sigma^2|F_o| + 0.000941|F_o|^2)$
$(\Delta/\sigma)_{\rm max}$ = 0.012
$\Delta\rho_{\rm max}$ = 0.586 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.251 e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Data collection: Enraf-Nonius CAD-4 software. Data reduction: Enraf-Nonius CAD-4 software; data were corrected for

Lp effects. Program(s) used to solve structure: *MULTAN*11/84 (Main, Germain & Woolfson, 1984). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976). H atoms from difference Fourier synthesis and refined isotropically. Molecular graphics: *SCHAKAL* (Keller, 1988). Software used to prepare material for publication: *PARST* (Nardelli, 1983).

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

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Ni	1	0.02797 (9)	$\frac{3}{4}$	3.67 (2)
N1	0.9315 (3)	−0.1288 (4)	0.6792 (3)	3.99 (12)
N2	0.8664 (3)	0.0104 (4)	0.8148 (3)	3.92 (10)
N3	0.9497 (3)	0.1683 (5)	0.6645 (4)	5.77 (16)
C11	0.9311 (4)	0.2517 (8)	0.6164 (4)	5.52 (19)
O1	0.9108 (4)	0.3413 (6)	0.5648 (4)	10.23 (22)
C1	0.9699 (4)	−0.2058 (7)	0.6146 (4)	4.63 (18)
C2	0.9249 (4)	−0.3158 (6)	0.5796 (4)	5.44 (18)
C3	0.8353 (5)	−0.3485 (7)	0.6091 (5)	5.75 (21)
C4	0.7940 (4)	−0.2722 (6)	0.6736 (5)	4.86 (17)
C5	0.8425 (3)	−0.1615 (5)	0.7072 (5)	3.75 (13)
C6	0.8038 (3)	−0.0754 (5)	0.7775 (4)	3.49 (13)
C7	0.7090 (4)	−0.0781 (6)	0.8054 (4)	4.88 (17)
C8	0.6801 (4)	0.0023 (7)	0.8727 (5)	6.15 (22)
C9	0.7441 (5)	0.0869 (7)	0.9116 (4)	5.65 (19)
C10	0.8370 (4)	0.0874 (6)	0.8820 (4)	5.03 (18)

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

Ni—N1	2.112 (4)	Ni—N2	2.116 (4)
Ni—N3	2.024 (5)	C11—O1	1.215 (9)
N3—C11	1.131 (9)		
N1—Ni—N2	77.3 (2)	N1—Ni—N3	90.8 (2)
N1—Ni—N1^{i}	86.1 (2)	N1—Ni—N2^{i}	95.8 (2)
N1—Ni—N3^{i}	169.9 (2)	N2—Ni—N3	92.9 (2)
N2—Ni—N2^{i}	170.6 (2)	N2—Ni—N3^{i}	93.5 (2)
N3—Ni—N1^{i}	169.9 (2)	N3—Ni—N3^{i}	93.9 (2)
Ni—N3—C11	172.8 (5)	N3—C11—O1	179.8 (7)

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

Table 3. *Distortion* Δ *of the* [NiN$_6$] *polyhedron in the* [Ni(bipy)$_2$(NCO)$_2$] *compound*

Δ has been calculated using the formula:

$$\Delta = \sum\frac{[\delta b_1 - \delta b_{1oct}]}{846} + \sum\frac{[\delta b_2 - \delta b_{2oct}]}{594} + \sum\frac{[\delta_i - \delta_{oct}]}{234}$$

Dihedral angle	Octahedron (°)	NiN$_6$ (°)	Trigonal prism (°)
$\delta b_{1.1}$	70.5	62.3 [N3'—N2—N1'—N1]	0
$\delta b_{1.2}$	70.5	75.6 [N1'—N2—N3'—N3]	0
$\delta b_{1.3}$	70.5	70.0 [N2'—N1—N3—N2]	0
$\delta b_{2.1}$	70.5	67.2 [N3'—N2—N3—N1]	120
$\delta b_{2.2}$	70.5	69.1 [N2'—N3'—N1'—N2]	120
$\delta b_{2.3}$	70.5	62.3 [N3—N2'—N1—N1']	120
δ_1	70.5	79.6 [N3'—N1'—N2'—N1]	90
δ_2	70.5	75.6 [N3'—N2'—N3—N1]	90
δ_3	70.5	72.6 [N2—N3—N3'—N2']	90
δ_4	70.5	67.2 [N3—N3'—N2'—N1']	90
δ_5	70.5	67.5 [N2—N1—N1'—N2']	90
δ_6	70.5	79.6 [N1'—N2—N1—N3]	90
Δ	0	0.11	1

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

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71431 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA1051]

References

Arriortua, M. I., Mesa, J. L., Rojo, T., Debaerdemaeker, T., Beltran, D., Stratemeier, H. & Reinen, D. (1988). *Inorg. Chem.* **27**, 2976–2982.

Cortés, R., Arriortua, M. I., Rojo, T., Mesa, J. L., Solans, X. & Beltrán, D. (1988). *Acta Cryst.* C**44**, 986–990.

Cortés, R., Arriortua, M. I., Rojo, T., Solans, X. & Beltrán, D. (1986). *Polyhedron*, **5**, 1987–1990.

Healy, P. C., Patrick, J. M. & White, A. H. (1984). *Aust. J. Chem.* **37**, 921–927.

Keller, E. (1988). *SCHAKAL88. Fortran Program for the Graphic Representation of Molecular and Crystallographic Models.* Univ. of Freiburg, Germany.

Lever, A. B. P., Mantovani, E. & Ramaswamy, B. S. (1971). *Can. J. Chem.* **49**, 1957–1961.

Main, P., Germain, G. & Woolfson, M. M. (1984). *MULTAN11/84. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Muetterties, E. L. & Guggenberger, L. J. (1974). *J. Am. Chem. Soc.* **96**, 1748–1756.

Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.

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

Tedenac, J. C. & Philippot, E. (1974). *Acta Cryst.* B**30**, 2286–2289.

Vía, J., Arriortua, M. I., Rojo, T., Mesa, J. L. & García, A. (1989). *Bull. Soc. Chim. Belg.* **98**, 179–182.

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Structures of Mixed Benzenethiolato–Phosphino Dinuclear Complexes of Nickel(II) and Palladium(II)

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Abstract

The structures of di-μ-benzenethiolato-bis{[1,2-bis(diphenylphosphino)ethane]nickel(II)} perchlorate acetonitrile solvate, [Ni$_2$(SPh)$_2$(dppe)$_2$](ClO$_4$)$_2$.2MeCN (1), and di-μ-benzenethiolato-bis-

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