Table 1. *Selected geometric parameters (Å, °) for (I) and (II)*

	(I)	(II)
Co—S1	2.1233 (11)	2.138 (2)
Co—S2	2.1266 (11)	2.135 (2)
S1—C1	1.705 (3)	1.713 (6)
S2—C2	1.702 (4)	1.725 (7)
S3—C1	1.733 (3)	1.741 (7)
S4—C2	1.738 (4)	1.739 (6)
S3—C3	1.714 (4)	1.719 (6)
S4—C3	1.728 (4)	1.725 (8)
S5—C3	1.661 (4)	1.657 (7)
C1—C2	1.377 (5)	1.352 (9)
Mean Co—C†	2.028 (12)	2.050 (7)
S1—Co—S2	93.20 (4)	93.65 (7)
C1—S1—Co1	103.14 (13)	102.3 (2)
C2—S2—Co2	103.30 (12)	102.3 (2)

† Estimated errors on averaged Co—C distances are calculated as $\sigma = [\Sigma(d_i - d_{mean})^2/(n-1)]^{1/2}$, $n = 5$.

Data for (II) were collected with an area detector (Stoe IPDS) with a crystal-to-plate distance of 80 mm ($\theta_{max} = 24.27°$), an exposure time of 5 min per plate, with φ varying from 0 to 200° by increments $\Delta\varphi = 3°$; the duration of measurement was 10 h. With respect to the ψ-scan absorption correction for (I), discrepancies between the resulting T_{max}/T_{min} values and those expected from the μ value and crystal size might be attributable to the very thin shape of the crystal, which makes an accurate determination of the smallest crystal dimension difficult. H atoms were introduced at calculated positions, included in structure-factor calculations and not refined (riding model). In the final electron-density map of (II), the strongest negative density peak was found to be -1.45 e Å^{-3} in the vicinity (1 Å) of the Co atom. Two C atoms (C6 and C7) of the Cp ring in (I) exhibit strongly anisotropic displacement parameters ($U_3/U_1 = 12$), but attempts to introduce a disorder model for the Cp ring were unsuccessful.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994) for (I); *EXPOSE* (Stoe & Cie, 1995) for (II). Cell refinement: *CAD-4 EXPRESS* for (I); *SELECT* (Stoe & Cie, 1995) for (II). Data reduction: *XCAD-4* (Harms, 1993) for (I); *INTEGRATE* (Stoe & Cie, 1995) for (II). Program(s) used to solve structures: *SHELXS86* (Sheldrick, 1990) for (I); *Xtal3.2* (Hall, Flack & Stewart, 1992) for (II). Program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993) for (I); *Xtal3.2* for (II). For both compounds, molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93* for (I); *Xtal3.2* for (II).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AB1475). Services for accessing these data are described at the back of the journal.

References

Armstrong, E. M., Austerberry, M. S., Beddoes, R. L., Helliwell, M., Joule, J. A. & Garner, C. D. (1993). *Acta Cryst.* C49, 1764–1766.
Baird, H. W. & White, B. M. (1966). *J. Am. Chem. Soc.* 88, 4744–4745.
Canadell, E., Ravy, S., Pouget, J.-P. & Brossard, L. (1990). *Solid State Commun.* 75, 633–638.
Churchill, M. R. & Fennessey, J. P. (1968). *Inorg. Chem.* 7, 1123–1129.

Ellern, A., Bernstein, J., Becker, J. Y., Zamir, S., Shalal, L. & Cohen, S. (1994). *Chem. Mater.* 6, 1378–1385.
Enraf–Nonius (1994). *CAD-4 EXPRESS.* Version 5.1/1.2. Enraf–Nonius, Delft, The Netherlands.
Fourmigué, M. & Coulon, C. (1994). *Adv. Mater.* 6, 948–952.
Fourmigué, M., Lenoir, C., Coulon, C., Guyon, F. & Amaudrut, J. (1995). *Inorg. Chem.* 34, 4979–4985.
Guyon, F., Fourmigué, M., Audebert, P. & Amaudrut, J. (1995). *Inorg. Chim. Acta,* 239, 117–124.
Guyon, F., Lenoir, C., Fourmigué, M., Larsen, J. & Amaudrut, J. (1990). *Bull. Soc. Chim. Fr.* 131, 217–226.
Hall, S. R., Flack, H. D. & Stewart, J. M. (1992). Editors. *Xtal3.2 Reference Manual.* Universities of Western Australia, Australia, Geneva, Switzerland, and Maryland, USA.
Harms, K. (1993). *XCAD-4. Program for the Reduction of CAD-4 Diffractometer Data.* University of Marburg, Germany.
Hunter, C. A. & Sanders, J. K. M. (1990). *J. Am. Chem. Soc.* 112, 5525–5534.
Johnson, C. K. (1976). *ORTEPII.* Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Miller, E. J., Brill, T. B., Rheingold, A. L. & Fultz, W. (1983). *J. Am. Chem. Soc.* 105, 7580–7584.
Sheldrick, G. M. (1990). *Acta Cryst.* A46, 467–473.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Sheldrick, G. M. (1995). *SHELXTL/PC.* Version 5.04. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Stoe & Cie (1995). *IPDS. Imaging Plate Diffractometer System.* Stoe & Cie, Darmstadt, Germany.
Ushijima, H., Sudoh, S., Kajitani, M., Shimizu, K., Akiyama, T. & Sugimori, A. (1990). *Inorg. Chim. Acta,* 175, 11–12.
Ushijima, H., Sudoh, S., Kajitani, M., Shimizu, K., Akiyama, T. & Sugimori, A. (1991). *Appl. Organomet. Chem.* 5, 221–228.
Werner, H., Xiaolan, L. & Nurnberg, O. (1992). *Organometallics,* 11, 432–436.

Bis(2,2'-bipyridine-N,N')(tricyanomethanido-N)copper(II) Tricyanomethanide

IVAN POTOČŇÁK,[a] MICHAL DUNAJ-JURČO,[a] DUŠAN MIKLOŠ[a] AND LOTHAR JÄGER[b]

[a]*Department of Inorganic Chemistry, Slovak Technical University, Radlinského 9, 812 37 Bratislava, Slovakia, and* [b]*Institut of Inorganic Chemistry, Martin-Luther-University, Halle-Wittenberg, Weinbergweg 16, 06120 Halle/Saale, Germany. E-mail: potocnak@cvtstu.cvt.stuba.sk*

Abstract

The crystal structure of $[Cu\{C(CN)_3\}(C_{10}H_8N_2)_2]$-$[C(CN)_3]$ is formed by discrete $[Cu(bipy)_2\{C(CN)_3\}]^+$ cations and $[C(CN)_3]^-$ anions (bipy is 2,2'-bipyridine). The coordination polyhedron of Cu^{II} is a distorted trigonal bipyramid with a $\{CuN_5\}$ chromophore.

Comment

The non-linear pseudohalogenides $[N(CN)_2]^-$, $[ONC(CN)_2]^-$ and $[C(CN)_3]^-$ $\{tcm^- = [C(CN)_3]^-\}$ are known to have a good coordination ability. Contrary to this fact, in our previous works using the phenanthroline (phen) molecule as a neutral ligand and the above anions, we have been able to prepare compounds only with $[N(CN)_2]^-$ (Potočňák, Dunaj-Jurčo, Mikloš & Jäger, 1996; Potočňák, Dunaj-Jurčo, Mikloš, Kabešová & Jäger, 1995) and $[ONC(CN)_2]^-$ anions coordinated in the inner coordination sphere (Mikloš, Potočňák, Dunaj-Jurčo & Jäger, 1997). Thus, tricyanomethanide (tcm^-) always stayed in the outer coordination sphere and no coordination of tcm^- in combination with phen has been observed even in the case of the tcm^- anion being the only anionic ligand in the reaction mixture. We suppose the reason is a steric repulsion between the bulky tcm^- anion and the bulky and rigid phen ligand. We therefore decided to replace the phen ligand by the smaller and more flexible bipy ligand. The aim was to find out whether a compound with a coordinated tcm^- anion would be formed or not. The preparation resulted in the fivefold-coordinated title compound, (I), and the crystal structure is presented here.

(I)
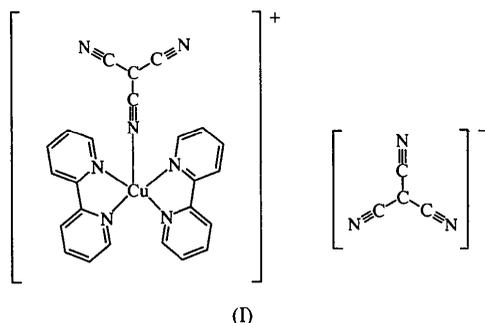
The labelling scheme of one formula unit is shown in Fig. 1. The Cu atom is fivefold coordinated by four N atoms of the two bipy molecules and one N atom of the $C(CN)_3^-$ ligand (in the equatorial plane). The coordination polyhedron is a distorted trigonal bipyramid. The second tcm^- anion does not enter the inner coordination sphere. The bond distances in the trigonal bipyramid are substantially different from those in the related compounds with the phen ligand. The two out-of-plane Cu—N10 and Cu—N30 distances in (I) have similar values [1.982 (3) and 1.954 (3) Å, respectively] (in phen compounds they are almost equal) and the bonds are almost collinear [N30—Cu—N10 175.73 (11)°]. The two in-plane distances (Cu—N20 and Cu—N40) have similar values too [2.104 (3) and 2.043 (3) Å, respectively], but they are longer on average than the out-of-plane Cu—N distances by 0.106 Å (the same feature as in phen compounds). The third in-plane Cu—N4 [N from the $C(CN)_3$ ligand] distance of 1.993 (3) Å is significantly shorter than the other two in-plane distances, but

is longer than the out-of-plane bonds. In phen compounds, this is always the shortest bond in the coordination polyhedron. The out-of-plane angles lie within the range 79.34 (11)–95.70 (12)° (similar to phen compounds). The bond angles in the equatorial plane of (I) differ considerably from the ideal trigonal angle of 120°, with one large angle of 137.14 (11)° (α_1 = N4—Cu—N40) and two small angles of 115.98 (11) (α_2 = N4—Cu—N20) and 106.87 (10)° (α_3 = N40—Cu—N20). Thus, the angle α_3 is narrower than the ideal angle of 120° by 13.13°, and there is a difference of 21.16° between α_1 and α_2. According to the criteria of Harrison & Hathaway (1980), the coordination polyhedron around the Cu atom can be best described as intermediate between trigonal-bipyramidal and square-pyramidal forms. According to the values of the angles α_1, α_2 and α_3 for pentacoordinated compounds with two phen molecules, their coordination polyhedra can be best described as trigonal bipyramidal with near C_{2v} symmetry. This difference in the shape of coordination polyhedra of (I) and of the phen compounds could be explained by larger dimensions of tcm^- in comparison with coordinated non-linear $[N(CN)_2]^-$ and linear pseudohalogenides $(CN^-$ and $NCS^-)$. The sum of the bond angles in the equatorial plane of the title compound (359.99°) indicates coplanarity of the Cu atom with the three equatorial atoms [the deviation of the Cu atom from the N4—N20—N40 plane is 0.013 (1) Å towards N30].
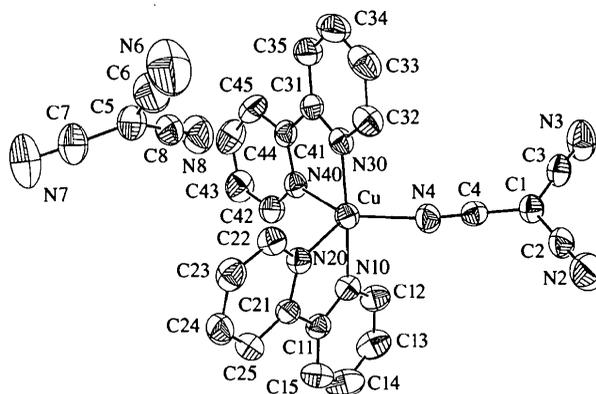
Fig. 1. *ORTEP* (Johnson, 1965) drawing of the formula unit showing the labelling of atoms. Displacement ellipsoids are plotted at the 40% probability level.

Owing to steric considerations in the trigonal-bipyramidal polyhedron, the N atoms of the bipy molecules are coordinated both in equatorial and axial positions. Both bipy molecules are almost planar [the largest deviation of atoms from the mean planes is 0.102 (6) Å]. The mean planes of the two bipy molecules are inclined at 77.89 (8)°. Aromatic bond distances of both bipy molecules are quite normal and range from 1.324 (4) to 1.346 (4) Å for N—C bonds and from 1.345 (6) to 1.381 (5) Å for C—C bonds, single

C—C bonds being 1.463 (4) and 1.463 (5) Å. The values of the bond angles within each pyridine ring of both bipy molecules range from 118.5 (4) to 123.2 (4)°, while the angles around the C—C σ-bond between the two pyridine rings lie in a somewhat larger range.

Both tcm⁻ anions are almost planar [the largest deviation of atoms from the mean plane being 0.014 (3) and 0.013 (5) Å for the coordinated and uncoordinated anion, respectively]. The mode of bonding in the tcm⁻ anion can be described as a largely delocalized π-bonding system (Golub, Köhler & Skopenko, 1986). According to this assumption, the C—C lengths around the central C1 and C5 atoms are the same within 2σ for both anions [on average 1.391 (5) Å], and they are considerably shorter than single C_{sp^2}—C_{sp} bonds (1.440 Å). Although the triple C≡N bond lengths are the same within 1σ for both anions [on average 1.135 (4) Å], contrary to the above assumption, they are slightly shorter than normal C≡N triple-bond lengths (1.153 Å). The angles around the central C atoms are close to the ideal value of 120°, while the C1—CX≡NX (X = 2, 3, 4) and C5—CX≡NX (X = 6, 7, 8) angles are almost linear.

Experimental

Crystals were prepared by mixing 1 ml of 1 *M* water solution of Cu(NO₃)₂ with 20 ml of 0.1 *M* methanol solution of bipy. 20 ml of 0.1 *M* water–methanol (1:1) solution of KC(CN)₃ was added. Dark-green crystals of the title complex appeared on the following day.

Crystal data

[Cu(C₄N₃)(C₁₀H₈N₂)₂]-(C₄N₃)	Mo $K\alpha$ radiation
M_r = 556.05	λ = 0.71073 Å
Monoclinic	Cell parameters from 25
$P2_1/c$	reflections
a = 14.530 (6) Å	θ = 5.85–11.63°
b = 13.290 (6) Å	μ = 0.886 mm⁻¹
c = 14.231 (6) Å	T = 293 (2) K
β = 110.31 (3)°	Prism
V = 2577.2 (19) Å³	0.70 × 0.40 × 0.25 mm
Z = 4	Dark green
D_x = 1.433 Mg m⁻³	
D_m = 1.406 Mg m⁻³	
D_m measured by flotation in CCl₄–benzene	

Data collection

Syntex $P2_1$ diffractometer	R_{int} = 0.044
θ–2θ scans	θ_{max} = 25.07°
Absorption correction:	h = −17 → 16
ψ scan (North, Phillips & Mathews, 1968)	k = −15 → 0
	l = 0 → 16
T_{min} = 0.667, T_{max} = 0.801	3 standard reflections
4760 measured reflections	every 100 reflections
4573 independent reflections	intensity decay: <3%
2685 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max}$ = 0.001
$R[F^2 > 2\sigma(F^2)]$ = 0.036	$\Delta\rho_{max}$ = 0.223 e Å⁻³
$wR(F^2)$ = 0.115	$\Delta\rho_{min}$ = −0.281 e Å⁻³
S = 0.662	Extinction correction: none
4572 reflections	Scattering factors from
416 parameters	*International Tables for*
All H atoms refined	*Crystallography* (Vol. C)
$w = 1/[\sigma^2(F_o^2) + (0.0798P)^2]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. *Selected geometric parameters (Å, °)*

Cu—N30	1.954 (3)	C3—N3	1.132 (5)
Cu—N10	1.982 (3)	C4—N4	1.138 (4)
Cu—N4	1.993 (3)	C5—C6	1.387 (6)
Cu—N40	2.043 (3)	C5—C8	1.384 (5)
Cu—N20	2.104 (3)	C5—C7	1.392 (5)
C1—C4	1.393 (5)	C6—N6	1.139 (6)
C1—C2	1.397 (5)	C7—N7	1.138 (5)
C1—C3	1.391 (5)	C8—N8	1.131 (4)
C2—N2	1.131 (5)		
N30—Cu—N10	175.73 (11)	C2—C1—C3	121.0 (3)
N30—Cu—N4	92.56 (12)	N2—C2—C1	179.6 (5)
N10—Cu—N4	91.26 (12)	N3—C3—C1	178.8 (4)
N30—Cu—N40	80.19 (12)	N4—C4—C1	178.3 (4)
N10—Cu—N40	95.70 (12)	C4—N4—Cu	171.0 (3)
N4—Cu—N40	137.14 (11)	C6—C5—C8	119.7 (4)
N30—Cu—N20	100.66 (11)	C6—C5—C7	120.7 (4)
N10—Cu—N20	79.34 (11)	C8—C5—C7	119.6 (4)
N4—Cu—N20	115.98 (11)	N6—C6—C5	179.1 (6)
N40—Cu—N20	106.87 (10)	N7—C7—C5	177.8 (5)
C4—C1—C2	119.1 (3)	N8—C8—C5	178.4 (4)
C4—C1—C3	119.9 (3)		

Intensities were corrected for Lorentz and polarization factors using *XP*21 (Pavelčík, 1993). The structure was solved by direct methods with *SHELXS*86 (Sheldrick, 1985) and subsequent Fourier syntheses using *SHELXL*93 (Sheldrick, 1993). Anisotropic displacement parameters were refined for all non-H atoms. All H atoms were located from the difference Fourier map and refined with free isotropic displacement parameters. Geometrical analysis was performed using *PARST* (Nardelli, 1983) and *SHELXL*93. *ORTEP* (Johnson, 1965) was employed to draw the ellipsoid plot.

Data collection: Syntex *P*21 software. Cell refinement: Syntex *P*21 software. Data reduction: *XP*21. Software used to prepare material for publication: *SHELXL*93.

References

Golub, A. M., Köhler, H. & Skopenko, V. V. (1986). In *Chemistry of Pseudohalogenides*. Amsterdam: Elsevier.

Harrison, W. D. & Hathaway, B. J. (1980). *Acta Cryst.* B36, 1069–1074.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

Mikloš, D., Potočňák, I., Dunaj-Jurčo, M. & Jäger, L. (1997). *Acta Cryst. C*. Accepted for publication.

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

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.

Pavelčík, F. (1993). *XP21. A Computer Program for Syntex P2₁ Data Reduction.* Comenius University, Bratislava, Slovakia.

Potočňák, I., Dunaj-Jurčo, M., Mikloš, D. & Jäger, L. (1996). *Acta Cryst.* **C52**, 1653–1655.

Potočňák, I., Dunaj-Jurčo, M., Mikloš, D., Kabešová, M. & Jäger, L. (1995). *Acta Cryst.* **C51**, 600–602.

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.

4:1 Lewis Base Adducts of Palladium Dichloride: [Pd(3-picoline)4]Cl2.2H2O

Wei Chen,[a] Cai-ming Liu,[b] Ren-gen Xiong[b] and Xiao-zeng You[b]

[a]*Department of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia, and* [b]*Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Nanjing University, Centre for Advanced Studies in Science and Technology of Microstructure, Nanjing 210093, People's Republic of China. E-mail: chenwei@kimia.um.edu.my*

Abstract

The palladium ion of the title 4:1 Lewis base adduct, tetrakis(3-methylpyridine-N)palladium(II) dichloride dihydrate, [Pd(C₆H₇N)₄]Cl₂.2H₂O, is coordinated to four 3-methylpyridine ligands in a planar configuration with an average Pd—N distance of 2.024 (2) Å. Two chloride ions are in *trans* positions at a distance of 3.671 (2) Å from the palladium ion. The water molecules are each disordered over two sites with half occupancy.

Comment

Studies of palladium complexes in organic synthesis and catalytic processes, as well as studies of their chemical reactivity, spectroscopy and structural aspects have received great attention (Newkome *et al.*, 1985). Palladium(II) complexes possessing simple N-atom donors are well documented in the literature (Hartley, 1981) and a number of structural studies have been reported on these complexes. However, to the best of our knowledge, few examples of 4:1 Lewis base adducts of

palladium such as (4-ClC₅H₄N)₄Pd(C₅HF₆O₂)₂ have been characterized by single-crystal X-ray diffraction (Siedle & Pignolet, 1982). These palladium complexes were found to possess special uses in *ortho*-metallation (Siedle, 1981*a*), β-diketonate transfer reactions (Siedle, 1981*b*) and acid–base surface complexes formed by utilizing metal oxides as condensed-phase donor (Siedle, Sperl & Rusch, 1980; Siedle & Newmark, 1981). In this paper, we report the crystal structure of another 4:1 Lewis base adduct of palladium, namely, the 3-methylpyridine adduct [(3-picoline)₄Pd]Cl₂.2H₂O, (I).

(I)
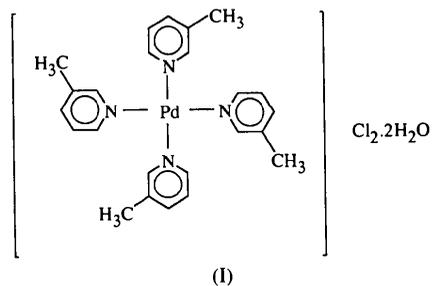
The geometry and the numbering scheme of the title compound is presented in Fig. 1. The Pd atom is coordinated to four picoline ligands in a square-planar arrangement and lies on a centre of symmetry. Weak contacts to two chloride ions, at distances of 3.671 (2) Å from the Pd atom, define the axial positions of a grossly tetragonally distorted octahedron. The angles subtended by the two chlorides to N1 and N2 are 91.7 (1) and 88.3 (1), and 91.2 (1) and 88.8 (1)°, respectively. Similar distortion is also ob-
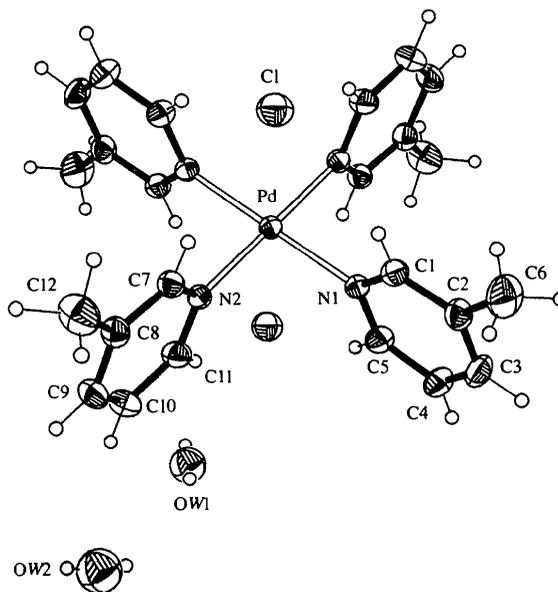
Fig. 1. *ORTEP* (Sheldrick, 1990*b*) plot drawn at the 30% probability level. H atoms are drawn as spheres of arbitrary radii.