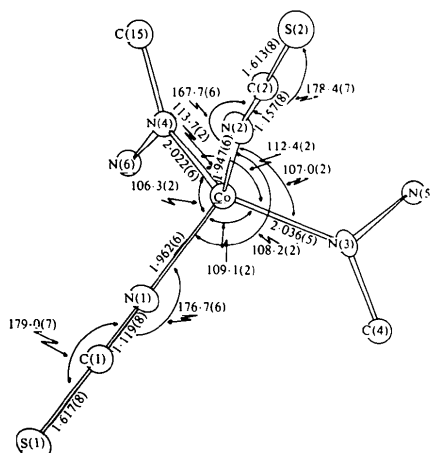Fig. 1. Molecular structure and numbering scheme.

Fig. 2. Interatomic distances (Å) and angles (°) around the central ion, with their e.s.d.'s.

are coordinated to the Co through N(1) and N(2), completing a distorted tetrahedron. The coordination around the Co atom is shown in Fig. 1. All relevant distances and angles are shown in Fig. 2. The two rings

of each organic ligand are planar within one e.s.d. The mean value of the dihedral angle between phenyl and pyrazole rings is 72·95°. In the complex $[Ag(C_{11}H_{12}N_2)_3]NO_3$ (Francisco, Mascarenhas & Lechat, 1979) which contains the same ligand, the value for the dihedral angle is 57·4°. The difference is probably due to the shorter coordination radius of Co which brings the ligand molecules closer together than in the Ag complex causing greater steric hindrance. All other distances and angles agree within 3σ with the values found in tris(3,5-dimethyl-1-phenylpyrazole)silver(I) nitrate, and in bis(3,5-dimethyl-1-phenylpyrazole)-dinitratocopper(II) (Francisco, Lechat & Mascarenhas, 1979).

References

FRANCISCO, R. H. P., LECHAT, J. R. & MASCARENHAS, Y. P. (1979). Acta Cryst. B35, 1468–1469.
FRANCISCO, R. H. P., MASCARENHAS, Y. P. & LECHAT, J. R. (1979). Acta Cryst. B35, 177–178.
GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). Acta Cryst. A27, 368–376.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
JOHNSON, C. K. (1965). ORTEP. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
MASSABNI, A. C. (1979). Personal communication.

Potassium Dicyanoaurate(I)–2,2′-Bipyridyl

By PETER G. JONES, WILLIAM CLEGG AND GEORGE M. SHELDRICK

Anorganisch Chemisches Institut der Universität Göttingen, Tammannstrasse 4, 3400 Göttingen, Federal Republic of Germany

Abstract. $K[Au(CN)_2].C_{10}H_8N_2$, $M_r = 444·29$, monoclinic, $P2_1$, $a = 3·789$ (1), $b = 18·871$ (6), $c = 9·293$ (3) Å, $\beta = 101·73$ (2)°, $U = 650·6$ Å^3, $Z = 2$, $D_x = 2·27$ Mg m^{-3}, μ(Mo $K\alpha$) = 11·6 mm^{-1}. $R = 5·4\%$ for 2140 unique reflexions. The structure consists of K$^+$ and linear $[Au(CN)_2]^-$ ions and bipyridyl molecules which are not coordinated to Au.

Introduction. Dothie, Llewellyn, Wardlaw & Welch (1939) prepared single crystals of a compound which

they formulated as K[Au(bpy)(CN)$_2$] (bpy = 2,2'-bipyridyl). The reported space group was $C222_1$, with $a = 18.15$, $b = 3.74$, $c = 18.74$ Å, $Z = 4$. The very short b axis would constrain the anion to be approximately planar, an unexpected geometry for four-coordinate Au^I. We therefore decided to undertake a structure determination.

Crystals in the form of colourless needles were obtained by the method of Dothie *et al.* (1939). They decomposed rapidly under the combined influence of air and X-rays, but were reasonably stable when sealed in glass capillaries. A crystal $0.35 \times 0.2 \times 0.15$ mm was used to collect a hemisphere of data ($5 < 2\theta < 50°$) on a Stoe four-circle diffractometer with monochromated Mo $K\alpha$ radiation. Three repeatedly monitored check reflexions decreased in intensity by about 25% during data collection, and other reflexions were scaled accordingly. 4913 reflexions were measured. Orthorhombic cell dimensions $a = 18.200$ (6), $b = 3.789$ (1), $c = 18.869$ (6) Å were obtained by least squares from accurate centring of 24 strong reflexions between $2\theta = 15$ and $27°$.

Attempts to solve the structure in $C222_1$ were unsuccessful, and the merging R for equivalent reflexions was high (12% after Lp and absorption corrections). The data reduction was repeated in a monoclinic cell, space group $P2_1$, derived from the $C222_1$ cell by the matrix [010/001/0.5 −0.5 0]. After application of

Table 1. *Atomic coordinates* ($\times 10^4$) *and isotropic temperature factors* (Å$^2 \times 10^3$)

	x	y	z	U
Au	−210 (2)	5000	−232 (1)	46†
K	5380 (14)	7418 (3)	2488 (5)	58†
C(1)	−599 (67)	5990 (15)	408 (29)	72 (7)
C(2)	−160 (56)	3990 (11)	−1003 (23)	48 (5)
N(1)	−757 (52)	6551 (11)	898 (21)	62 (5)
N(2)	5 (53)	3477 (10)	−1550 (21)	64 (5)
N(11)	4152 (39)	6360 (7)	4416 (14)	74 (6)
C(12)	3366 (39)	6474 (7)	5801 (14)	52 (5)
C(13)	3182 (39)	5901 (7)	6733 (14)	73 (7)
C(14)	3784 (39)	5215 (7)	6280 (14)	67 (7)
C(15)	4569 (39)	5101 (7)	4896 (14)	78 (6)
C(16)	4753 (39)	5673 (7)	3964 (14)	72 (7)
N(21)	1540 (35)	7653 (8)	5066 (11)	63 (5)
C(22)	2784 (35)	7195 (8)	6238 (11)	53 (5)
C(23)	3173 (35)	7437 (8)	7680 (11)	19 (3)
C(24)	2317 (35)	8137 (8)	7950 (11)	94 (9)
C(25)	1073 (35)	8595 (8)	6778 (11)	95 (9)
C(26)	684 (35)	8353 (8)	5336 (11)	83 (8)

† Effective isotropic U derived from the following anisotropic temperature factors (Å$^2 \times 10^3$):

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Au	59 (1)	38 (1)	41 (1)	3 (1)	10 (1)	−8 (1)
K	72 (3)	53 (3)	50 (3)	6 (2)	29 (3)	−4 (3)

The temperature-factor exponent takes the form: $-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^*)$.

Table 2. *Bond lengths* (Å) *and angles* (°)

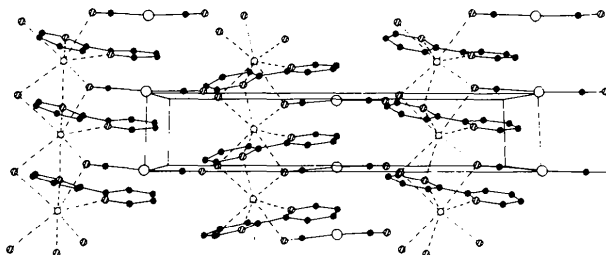| Au–C(1)	1.98 (4)	Au–C(2)	2.04 (4)
C(1)–N(1)	1.16 (5)	C(2)–N(2)	1.10 (5)
C(12)–C(22)	1.45 (5)		
C(1)–Au–C(2)	176 (2)	N(1)–C(1)–Au	175 (3)
N(2)–C(2)–Au	172 (3)	N(11)–C(12)–C(22)	119 (2)
C(13)–C(12)–C(22)	122 (2)	C(12)–C(22)–N(21)	115 (2)
C(12)–C(22)–C(23)	126 (2)		

Fig. 1. Packing diagram viewed down *c*. Large open circles represent Au, small open circles K, hatched circles N, and full circles C.

Lp and empirical absorption corrections, averaging equivalent reflexions gave 2154 reflexions, 2142 with $F > 4\sigma(F)$. The merging R for equivalent reflexions was 6%. The Au atom was located by a Patterson synthesis and other atoms were located by successive difference syntheses. Both location and refinement of light atoms proved difficult because of pseudosymmetry generated by the Au atom. The bipyridyl rings were constrained to be rigid hexagons with all bond lengths 1.395 Å. If this constraint was removed, rings with unrealistic distortions resulted; the major distortions were in the region of a previously obtained false image of the K atom. In view of the large e.s.d.'s of light-atom bond lengths, the hexagon model is justified (*cf.* C–C$_{av.}$ 1.39 Å, bond angles 117–124° in bpy itself: Merritt & Schroeder, 1956).

In the final stages of refinement a parameter x was refined to allow for extinction; it refined to 62 (3) $\times 10^{-8}$, where F_c is multiplied by $1 - xF^2/\sin\theta$. The final R and $R' = \sum w^{1/2}\Delta / \sum w^{1/2}|F_o|$ were 0.054. The weighting scheme was $w = 1/\sigma^2(F)$. Final atom coordinates are given in Table 1, bond lengths and angles in Table 2. Diagrams of the structure are given in Figs. 1 and 2.*

Discussion. The structure consists of K$^+$ and linear [Au(CN)$_2$]$^-$ ions, and bpy molecules which are not coordinated to Au, contrary to previous assumption.
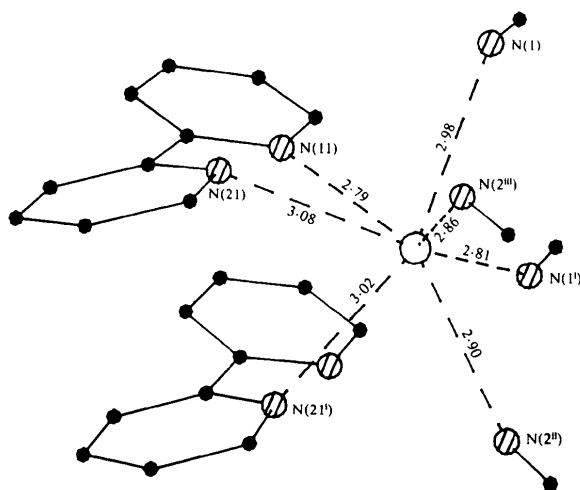
Fig. 2. Coordination about the K$^+$ ion. Distances are in Å (e.s.d.'s 0·04 Å). Symmetry transformations are: (i) 1+ x, y, z; (ii) 1 − x, $\frac{1}{2} + y, -z$; (iii) −$x, \frac{1}{2} + y, -z$.

This reflects the very strong tendency of Au^I to two-coordination; no four-coordinate Au^I species has been fully crystallographically characterized, although Cochran, Hart & Mann (1957) have established a distorted tetrahedral coordination in [Au{o-C$_6$H$_4$-(AsEt$_2$)$_2$}$_2$]I (where only Au, As and I atoms were located).

The [Au(CN)$_2$]$^-$ ion is essentially linear, as in K[Au(CN)$_2$] (Rosenzweig & Cromer, 1959). The Au—C and C—N distances are comparable with those in K[Au(CN)$_2$] [2·12 (4), 1·17 (20) Å] and in [AuCN(Ph$_3$P)] [1·85 (4), 1·25 (4) Å; Bellon, Manassero & Sansoni, 1969], but in all cases the presence of the Au atom makes light-atom bond lengths unreliable.

The K$^+$ ion is coordinated by seven N atoms, three from bpy molecules and four from —CN groups, at 2·79 to 3·08 Å (Fig. 2). The bpy molecules are distorted with respect to the free ligand, the dihedral angle between the rings being 24°.

References

Bellon, P. L., Manassero, M. & Sansoni, M. (1969). *Ric. Sci.* **39**, 173–175.
Cochran, W., Hart, F. A. & Mann, F. G. (1957). *J. Chem. Soc.* pp. 2816–2828.
Dothie, H. J., Llewellyn, F. J., Wardlaw, W. & Welch, A. J. E. (1939). *J. Chem. Soc.* pp. 426–428.
Merritt, L. L. Jr & Schroeder, E. D. (1956). *Acta Cryst.* **9**, 801–804.
Rosenzweig, A. & Cromer, D. T. (1959). *Acta Cryst.* **12**, 709–712.

trans-Bis(isothiocyanato)tetrakis(pyridin)kobalt(II)

Von Hans Hartl und Irene Brüdgam

Institut für Anorganische und Analytische Chemie der Freien Universität Berlin, Fabeckstrasse 34/36, D-1000 Berlin 33, Bundesrepublik Deutschland

Abstract. Co(C$_5$H$_5$N)$_4$(NCS)$_2$, C$_{22}$H$_{20}$CoN$_6$S$_2$, M_r = 491·5, monoclinic, $C2/c$, a = 12·461 (6), b = 12·910 (6), c = 16·509 (8) Å, β = 118·60 (5)°, V = 2331·8 Å^3, Z = 4, D_c = 1·399 Mg m^{-3}, μ(Mo $K\alpha$) = 0·95 mm^{-1}. Co is octahedrally coordinated to the N atoms of four pyridine and two *trans*-coordinated isothiocyanate ligands. The angle Co—N—CS is 155·9 (4)°.

Einleitung. Komplexverbindungen des Typs ML_4(NCS)$_2$ mit M = Co, Ni bilden mit einer Reihe von Gastmolekülen Chlathratverbindungen mit zeo-lithischen Eigenschaften, wenn der Ligand L ein geeignet substituiertes Pyridinmolekül, wie z.B. 4-

Methylpyridin = pic ist (Schaeffer, Dorsey, Skinner & Christian, 1957; Belitskus, Jeffrey, McMullan & Stephenson, 1963; Allison & Barrer, 1969). Die Stammverbindungen mit L = Pyridin = py geben keine Chlathratverbindungen, jedoch konnten davon stöchiometrisch aufgebaute Adduktverbindungen mit Akzeptormolekülen wie Jod und Jodoform dargestellt werden (Hartl & Steidl, 1977, 1980). Um den Einfluss der Akzeptormoleküle auf die Komplexverbindung, insbesondere auf die Thiocyanatgruppe, besser studieren zu können, wurde die vorliegende Strukturaufklärung durchgeführt.

Co(py)$_4$(NCS)$_2$ wurde nach der Vorschrift von Grossman & Hünseler (1905) hergestellt und aus