December, 1981] © *1981 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.*, **54**, *3861—3862 (1981)* 3861

The Crystal Structure of Dibromobis(iminodiacetamide)palladium(II)

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(Received April 22, 1981)

Synopsis. The crystals are triclinic, P$\bar{1}$. *R* is 0.047 for 1617 independent non-zero reflections. The complex has a centrosymmetric square-planar coordination, with two imino nitrogen and two bromine atoms in *trans* positions.

Iminodiacetamide, $HN(CH_2CONH_2)_2$ (abbreviation, idaaH_2), acts as a terdentate ligand to the copper(II)$^{1)}$ and nickel(II)$^{2)}$ atoms through one imino nitrogen and two amide oxygen atoms. However, the molecular structures of these two complexes are different, as is shown in Fig. 1. If some other transition metals are used, complexes with different structures can be expected. With this expectation, the palladium(II) complex has been prepared and its crystal structure has been analysed.

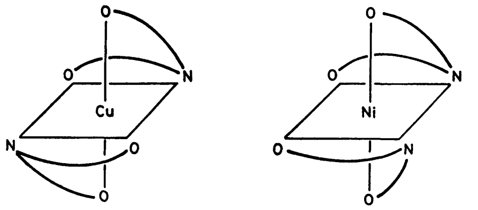

Fig. 1. The structures of $[Cu(idaaH_2)_2]^{2+}$ and $[Ni(idaaH_2)_2]^{2+}$.

Experimental

Preparation of the Complex. Palladium metal powder (0.5 g) was dissolved in an excess amount of a hot conc HBr–HNO_3 mixture (3 : 1 in volume). To this solution, an aqueous solution of 0.2 g of the ligand prepared by a method previously reported$^{1)}$ was added. The mixture was then kept at pH 2—3 by the use of an HBr or KOH solution, after which it was slowly cooled to room temperature until yellowish-brown plate crystals precipitated.

Measurement of Intensity Data. A crystal with dimensions of 0.1 mm × 0.1 mm × 0.1 mm was selected. The intensities were measured up to $2\theta=60°$ on a Philips PW1100 four-circle diffractometer with Mo *Kα* radiation monochromated by a graphite plate (θ-2θ scan). The 1617 independent reflections with $|F|>3\sigma$ were used with no corrections for absorption and extinction effects ($\mu r=0.3$).

Analytical and Crystal Data. Found: C, 17.92; H, 3.15; N, 15.49%. Calcd for $C_8H_{18}N_6O_4PdBr_2$: C, 18.18; H, 3.43; N, 15.90 %. F. W.=528.50. Triclinic, $a=9.694(2)$, $b=7.434(2)$, $c=6.505(2)$ Å, $\alpha=88.51(4)$, $\beta=101.34(4)$, $\gamma=71.50(2)°$. $U=434(1)$ Å^3. $D_x=2.02$ g/cm^3. $Z=1$. Space group P$\bar{1}$. $\mu=59.3$ cm^{-1} (Mo *Kα* radiation, $\lambda=0.7107$ Å).

Determination and Refinement of the Structure. The structure was determined by means of a heavy-atom method. The block-diagonal least-squares refinement was carried out with the weights of 1.0 for $|F_o|>1.3$ and 0.5 for the others. The positional parameters of all the hydrogen atoms obtained by means of a D-Fourier synthesis were refined with the isotropic temperature factors of 4.0 Å^2. The final *R* was 0.047. The atomic scattering factors were taken from Ref. 3, together with the anomalous scattering factors, *f′*, of the palladium and bromide ions. A FACOM M-160 computer at the Data Processing Center of Kanazawa University and a FACOM M-200 computer at the Computation Center of Nagoya University were used. The final atomic parameters are listed in Table 1.†

TABLE 1. THE FINAL ATOMIC PARAMETERS WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES ($\times 10^3$ FOR H's; $\times 10^4$ FOR OTHERS)

Atom	*x*	*y*	*z*	B_{eq}/Å^2 $^{5)}$
Pd	0	0	0	1.58(01)
Br	221(02)	−2463(02)	2653(02)	2.83(02)
N(1)	4069(12)	−2626(10)	−1440(13)	3.29(13)
O(1)	4059(07)	−3415(08)	1876(09)	2.28(08)
C(1)	3773(09)	−2207(10)	395(13)	1.96(10)
C(2)	3145(09)	−104(11)	685(13)	2.08(10)
N(3)	1912(07)	266(09)	1772(10)	1.83(08)
C(4)	1640(10)	2140(12)	2693(13)	2.40(10)
C(5)	2930(09)	2030(11)	4506(12)	2.05(10)
N(5)	3369(10)	3564(11)	4672(14)	3.45(12)
O(5)	3524(08)	590(09)	5717(10)	2.69(09)
Ha(N1)	441(10)	−391(10)	−183(10)	
Hb(N1)	420(10)	−214(10)	−224(10)	
Ha(C2)	396(10)	24(10)	158(10)	
Hb(C2)	252(10)	68(10)	−79(10)	
H(N3)	223(10)	−51(10)	270(10)	
Ha(C4)	132(10)	317(10)	162(10)	
Hb(C4)	63(10)	234(10)	312(10)	
Ha(N5)	414(10)	355(10)	576(10)	
Hb(N5)	222(10)	529(10)	344(10)	

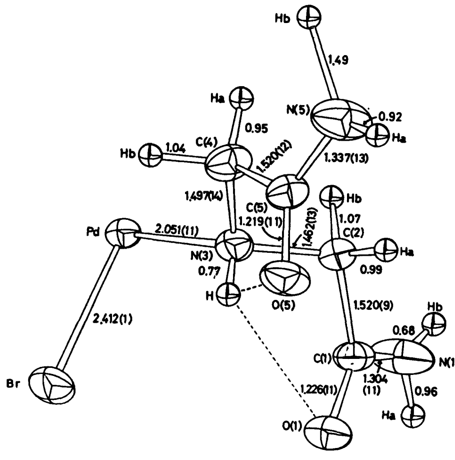

Fig. 2. Structure of the asymmetric unit with the bond lengths (*l*/Å) and the e.s.d.'s.
Thermal ellipsoids are drawn at 50% probability level.$^{4)}$ Hydrogen atoms are drawn as spheres with a diameter of 0.2 Å.

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† A table of the anisotropic temperature factors and a list of the observed and calculated structure amplitudes have been deposited with the Chemical Society of Japan (Document No. 8154).

Table 2. Bond angles $(\varphi/^\circ)$

Br-Pd-N(3)	87.3(3)	C(2)-C(1)-O(1)	120.3(7)
Pd-N(3)-C(2)	114.3(7)	N(1)-C(1)-O(1)	123.0(8)
Pd-N(3)-C(4)	112.3(7)	N(3)-C(4)-C(5)	110.0(8)
C(2)-N(3)-C(4)	110.8(9)	C(4)-C(5)-N(5)	116.8(8)
C(1)-C(2)-N(3)	111.2(7)	C(4)-C(5)-O(5)	120.3(8)
C(2)-C(1)-N(1)	120.3(7)	N(5)-C(5)-O(5)	122.9(9)

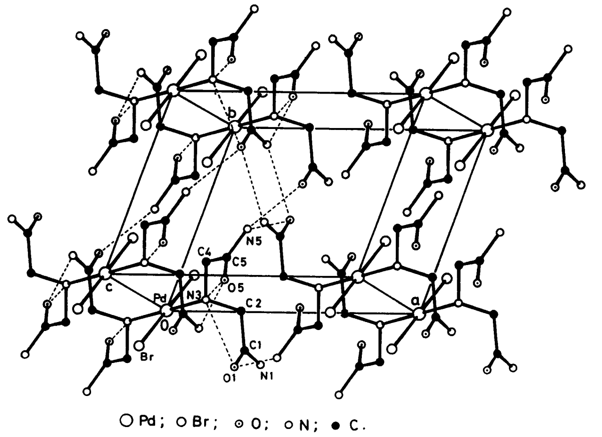

Fig. 3. Crystal structure. Dashed lines exhibit hydrogen bonds.

Description of the Structure

The molecular structure is shown in Fig. 2, along with the bond lengths. The bond angles are listed in Table 2.

The complex is square-planar, with the central atom lying on a center of symmetry of the triclinic unit cell. The bromide ions coordinate in *trans* positions of the square-plane so as to form a non-ionic complex. Each of the iminodiacetamide molecules acts as a unidentate ligand through the imino nitrogen atom; the two amide groups are uncoordinated. This coordination mode of the ligand molecule is different from that for the copper(II)[1] or nickel(II)[2] complex (Fig. 1). Details of the differences will be discussed elsewhere in comparison with other metal–iminodiacetamide complexes.

Table 3. Hydrogen bonds $(l/\text{Å})$

D —— H···A[a]	D-H	H-A	D-A
N(3)(x,y,z)H O(1)(x, y, z)	0.77	2.47	2.86
N(3)(x,y,z)H O(5)(x, y, z)	0.77	2.42	2.79
N(1)(x,y,z)Ha O(1)($1-x$, $-1-y$, $-z$)	0.96	2.08	2.98
N(1)(x,y,z)Hb O(5)(x, y, $-1+z$)	0.68	2.24	2.83
N(5)(x,y,z)Ha O(1)($1-x$, $-y$, $1-z$)	0.92	2.06	2.98
N(5)(x,y,z)Hb O(1)(x, $1+y$, z)	1.49	2.62	3.17
N(5)(x,y,z)Hb Br (x, $1+y$, z)	1.49	2.08	3.50

a) D, hydrogen donor; A, hydrogen acceptor.

The crystal structure is shown in Fig. 3. The hydrogen bonds are shown in this figure and also in Table 3.

The amide groups turn their oxygen atoms to the palladium atom, and a bifurcated intramolecular hydrogen bond is formed with the imino nitrogen atom, as is shown in Fig. 2 by dashed lines. The two amide nitrogen atoms approach the oxygen atoms of the neighboring molecules to form intermolecular hydrogen bonds in the directions of [1$\bar{1}$0], [100], [010], and [001]. The three-dimensional network is, thus, completed by these N–O-type hydrogen bonds. No contacts shorter than 3.5 Å are, however, observed around the bromine atom.

The author is grateful to Professor Seiji Sugiura of Kanazawa University for the use of the diffractometer.

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