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Acta Cryst. (1982). **B38**, 2239–2242

Structure of Potassium Azidopentacyanocobaltate(III) Dihydrate

BY E. E. CASTELLANO

Instituto de Física e Química de São Carlos, Universidade de São Paulo, Caixa Postal 369, 13.560, São Carlos, SP, Brazil

O. E. PIRO*† AND G. PUNTE†

Departamento de Física, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, 49 esquina 115, CC 67, 1900 La Plata, Argentina

AND J. I. AMALVY,‡ E. L. VARETTI† AND P. J. AYMÓNINO†

Departamento de Química, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, 47 esquina 115, 1900 La Plata, Argentina

(Received 10 December 1981; accepted 18 March 1982)

Abstract. $K_3[Co(CN)_5N_3] \cdot 2H_2O$, $M_r = 384.38$, triclinic, $P\bar{1}$, $a = 8.514(2)$, $b = 8.943(1)$, $c = 9.397(2)$ Å, $\alpha = 81.47(2)$, $\beta = 76.32(2)$, $\gamma = 75.95(1)^\circ$, $V = 671.3(3)$ Å³, $Z = 2$, $D_c = 1.902$, $D_m = 1.88(1)$ Mg m⁻³, Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å, $\mu(Mo K\alpha) = 2.13$ mm⁻¹, $F(000) = 380$. The structure was solved by Patterson methods and refined by full-matrix least squares with anisotropic temperature factors for all non-hydrogen atoms to final R factors of $R = 0.035$ and $R_w = 0.036$ for 1184 reflections. The structure shows a local plane of symmetry perpendicular to \mathbf{a} . The coordination around the Co^{III} ion is approximately octahedral with mean Co–C and Co–N distances of 1.89(2) and 2.005(5) Å respectively. The azide group is linear and asymmetric with the N–N bond nearer to the metal of length 1.204(7) Å and the other of length 1.156(7) Å.

Introduction. As part of a study of the hydrates of hexacoordinated pentacyanometallates (previous paper in this series: Della Vedova *et al.*, 1981, and references therein), the structure of potassium azidopentacyanocobaltate(III) dihydrate has been determined. The fact that this compound contains as a sixth ligand the azide ion adds further interest to the subject because only a few azido complexes have been thoroughly studied from the structural point of view.

The title compound was obtained as a polycrystalline powder by the reaction in aqueous solution of $[Co(NH_3)_5N_3] \cdot Cl_2$ (prepared as described in Linhard & Flygare, 1950) with KCN in the presence of added $CoCl_2 \cdot 6H_2O$ as a catalyst (Barca, Ellis, Tsao & Wilmarth, 1967). Ethanol was added to the resultant solution and the yellow powder obtained was separated by filtration. The product was recrystallized from water. Single crystals, in the form of small plates parallel to the (001) plane, were obtained by slow evaporation of an aqueous solution in the ice-box.

A prismatic crystal of approximate dimensions 0.1 × 0.1 × 0.2 mm was mounted on an Enraf–Nonius

* To whom correspondence should be addressed.
 † Member of the Carrera del Investigador Científico, CONICET, Argentina.
 ‡ Supported by a fellowship from CONICET, Argentina.

CAD-4 diffractometer. Cell dimensions and the orientation matrix for data collection were calculated by least squares from 16 centered reflections (with θ values in the range 6–21°) using graphite-monochromatized Mo $K\alpha$ radiation. Diffraction intensities for reflections having θ in the range 0–23° were measured by the ω - 2θ scan technique, using a variable scan speed (2.85–20° min⁻¹) determined by a fast prescan of 20° min⁻¹. The intensity of one standard reflection was essentially constant throughout the experiment. Of the 1686 independent reflections measured, 1184 having $I > 3\sigma(I)$ were used in the calculations. Data were corrected for Lorentz and polarization effects but not for absorption or extinction.

The Co^{III} and the three K⁺ ions were readily located from a Patterson map. A Fourier difference synthesis, phased on these atoms, showed all non-hydrogen atoms with the exception of the water O atoms which were found from a subsequent difference map. Anisotropic refinement using the minimization function $M = \sum w(|F| - |F_c|)^2$, with $w = 1/[\sigma^2(F) + c|F|^2]$ converged to final values of $R = 0.035$ and $R_w = 0.036$. The $\sigma(F)$ values were obtained from counting statistics and a c value of 0.0064 was determined by least squares. A final difference map was essentially flat except for a peak of about $1 \text{ e } \text{Å}^{-3}$ which turned out to correspond to a proton of one of the water molecules.

The scattering factors used were those given by Cromer & Waber (1974) and the anomalous-dispersion corrections (f') were those of Cromer & Ibers (1974). Most calculations were performed on a Vax computer with the *SHELX* system of programs (Sheldrick, 1976). The final positional parameters and equivalent

Table 1. Final positional coordinates and equivalent isotropic thermal parameters (Hamilton, 1959), with e.s.d.'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} (Å ²)
Co	0.2507 (1)	0.2414 (1)	0.2720 (1)	1.48 (4)
K(1)	0.1104 (2)	0.7155 (2)	0.3487 (1)	2.44 (7)
K(2)	0.6191 (2)	0.6981 (2)	0.3491 (1)	2.37 (7)
K(3)	0.2324 (2)	0.7188 (2)	-0.1585 (2)	3.27 (8)
C(1)	0.2709 (7)	0.3376 (6)	0.0812 (7)	1.7 (3)
C(2)	0.1321 (7)	0.1082 (6)	0.2284 (6)	1.8 (3)
C(3)	0.3678 (7)	0.3795 (6)	0.3146 (6)	1.7 (3)
C(4)	0.4549 (8)	0.0970 (7)	0.2161 (6)	2.2 (3)
C(5)	0.0435 (8)	0.3818 (7)	0.3223 (6)	2.0 (3)
N(1)	0.2836 (7)	0.3970 (6)	-0.0377 (6)	3.0 (3)
N(2)	0.0549 (7)	0.0311 (6)	0.2019 (6)	3.2 (3)
N(3)	0.4411 (6)	0.4611 (6)	0.3380 (6)	2.4 (3)
N(4)	0.5783 (7)	0.0080 (7)	0.1875 (6)	3.5 (3)
N(5)	-0.0855 (7)	0.4626 (6)	0.3508 (6)	2.8 (3)
N(6)	0.2250 (6)	0.1448 (6)	0.4805 (5)	2.3 (3)
N(7)	0.2572 (6)	0.0054 (6)	0.4972 (5)	2.0 (3)
N(8)	0.2872 (7)	-0.1284 (6)	0.5148 (6)	3.4 (3)
O(W1)	0.6490 (6)	0.2455 (6)	-0.1061 (6)	4.5 (3)
O(W2)	0.0362 (7)	0.2360 (7)	-0.1110 (6)	4.9 (3)

isotropic temperature factors calculated as described by Hamilton (1959) are given in Table 1.* The atom labeling and intramolecular bond distances in the anion are given in Fig. 1, which shows a projection down the normal to the (001) plane. Corresponding bond angles

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36805 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Intramolecular bond angles (°) in the anion, with e.s.d.'s in parentheses

C(1)—Co—C(2)	90.8 (2)	C(3)—Co—N(6)	90.4 (2)
C(1)—Co—C(3)	88.5 (2)	C(4)—Co—C(5)	177.6 (2)
C(1)—Co—C(4)	90.7 (2)	C(4)—Co—N(6)	91.0 (2)
C(1)—Co—C(5)	88.3 (2)	C(5)—Co—N(6)	90.1 (2)
C(1)—Co—N(6)	178.0 (2)	Co—C(1)—N(1)	179.8 (5)
C(2)—Co—C(3)	178.9 (2)	Co—C(2)—N(2)	177.6 (5)
C(2)—Co—C(4)	91.0 (2)	Co—C(3)—N(3)	178.5 (5)
C(2)—Co—C(5)	86.9 (2)	Co—C(4)—N(4)	177.6 (5)
C(2)—Co—N(6)	90.3 (2)	Co—C(5)—N(5)	177.0 (5)
C(3)—Co—C(4)	89.9 (2)	Co—N(6)—N(7)	116.3 (3)
C(3)—Co—C(5)	92.2 (2)	N(6)—N(7)—N(8)	179.3 (6)

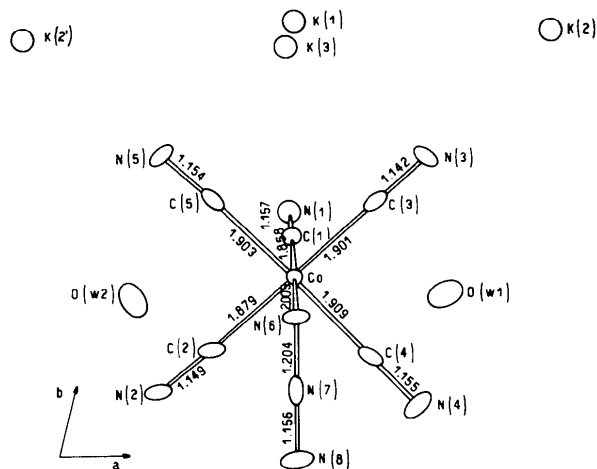


Fig. 1. Projection of the molecule down c^* , showing atom labeling and intramolecular bond distances (Å) in the anion. Estimated standard deviations are 0.005–0.007 Å. The K⁺ ion K(2') is related by symmetry to K(2) through a unit-cell translation along a .

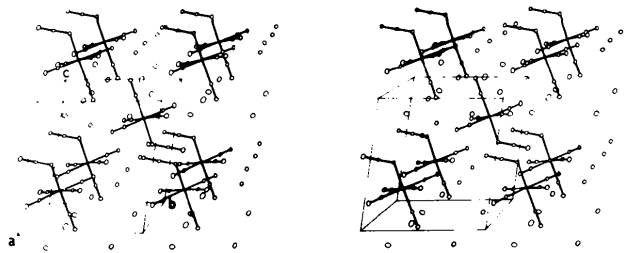


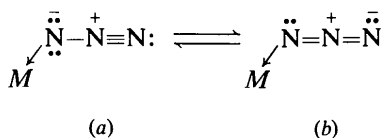
Fig. 2. Stereoscopic view of the structure down a^* . K⁺ ions are readily identified by having smaller thermal vibration ellipsoids than those corresponding to the water molecules.

are given in Table 2. The stereoscopic view of the structure, down the normal to the (100) plane, shown in Fig. 2, was drawn by the program *ORTEP* (Johnson, 1965) incorporated in the Enraf-Nonius structure determination package.

Discussion. It can be seen from Fig. 1 and Table 2 that the coordination around the central ion is approximately octahedral. The Co—C [mean: 1.89 (2) Å] and the C—N bond lengths [mean: 1.151 (6) Å] are in agreement with the corresponding values reported by Curry & Runciman (1959) for potassium hexacyanocobaltate(III).

The azide group is linear and asymmetric with N—N bond lengths of 1.204 (7) (the nearer to the metal) and 1.156 (7) Å (the farther). These bond lengths should be compared with the N—N distance reported for the symmetric azide ion which averages 1.154 (15) Å (Yoffe, 1966), and with typical N—N distances in covalent azides (HN₃ and organic azides) which are 1.248 (9) and 1.122 (9) Å, respectively (Cruickshank, Filippini & Mills, 1972).

The observed difference between the two N—N distances, and the Co—N—N bonding angle of 116.3 (3)°, which is between the values expected for *sp*³ (109.5°) and *sp*² (120°) hybridization of (bonded-to-metal) N, point to a contribution from the mesomeric structures (a) and (b):



Two different N—N distances have also been found in most of the azide complexes already studied, although bonding angles are in general closer to 120° and even larger than the presently reported value (Dori & Ziolo, 1973; de Gil, de Burguera, Rivera & Maxfield, 1977; Restivo, Ferguson, Hay & Piplani, 1978; Fawcett, Peacock & Russel, 1980).

A comparison with the structural data of azido complexes of Co^{III} shows that an increase in the Co—N distance is accompanied roughly by a decrease in the Co—N—N angle. This observation can be

rationalized assuming that a decreasing Co—N interaction turns the azide ligand in a similar way to the free ion. The repulsion between the electron lone pairs of the bonded azide should increase as the bonding pair becomes less engaged in the bond with the metal atom, increasing therefore the angle between the electron pairs and decreasing the Co—N—N angle. It can be seen also as a result of a comparison limited to complexes with only one azide ligand (for which the uncertainties in the measurements are relatively small) that the two N—N distances are increasingly similar with increasing Co—N bond distances (Table 3). The relatively long Co—N bond observed in [Co(CN)₅N₃]³⁻, as compared with the other complexes in Table 3, could be related to the negative charge of the anion. No π bonding exists between the Co atom and the azide ligand in these complexes (Gutterman & Gray, 1971).

In other complexes the azide ligand is coplanar with the metal ion, for example: [Co(NH₃)₅N₃](N₃)₂ (Palenik, 1964), *trans*-[Cu(NH₃)₂(N₃)₂] (Agrell, 1966), Cu(N₃)₂ (Söderquist, 1968) and [Co(tetraen)N₃](NO₃)₂·H₂O [tetraen = 4-(2-aminoethyl)-1,4,7,10-tetraazadecane] (Maxwell, 1971). In contrast, for K₃[Co(CN)₅N₃].2H₂O, the azide group, the central ion and the axial cyanide group lie, within experimental accuracy, on a plane perpendicular to **a**. This plane bisects the equatorial NC—Co—CN bond angles and constitutes a local, noncrystallographic mirror plane of the molecules (see Fig. 1). This mirror plane gives rise to the pseudo *m* symmetry displayed in the layers with *h* even of the weighted reciprocal lattice where the sampling points of the molecular Fourier transform happen to lie, approximately, on a line perpendicular to the local mirror plane.

The shortest distance between the O of a water molecule and a possible hydrogen-bond acceptor is 3.03 (2) Å [O(W1)···N(1) distance], suggesting that no strong H bonding exists in the crystal. This is in agreement with spectroscopic (IR) results (Amalvy, Varetto, Aymonino, Castellano, Piro & Punte, 1982).

The stereoscopic view of the structure shows that the azide groups are packed in an eclipsed antiparallel fashion forming stacks along **a** at intervals of approximately *a*/2 due to the particular location of the complex anion.

Table 3. A comparison of bonding parameters in selected azido complexes, with *e.s.d.*'s in parentheses

	Co—N(6) (Å)	N(6)—N(7) (Å)	N(7)—N(8) (Å)	δ (N—N)* (Å)	\angle Co—N(6)—N(7) (°)
[Co(NH ₃) ₅ N ₃] ²⁺ (a)	1.943 (5)	1.208 (7)	1.145 (7)	0.063	125.2 (2)†
[Co(tetraen)N ₃] ²⁺ (b)	1.957 (6)	1.209 (7)	1.152 (7)	0.057	119.0 (5)
[Co(CN) ₅ N ₃] ³⁻ (c)	2.005 (5)	1.204 (7)	1.156 (7)	0.048	116.3 (3)

References: (a) Palenik (1964). (b) Maxwell (1971). (c) This work.

* δ (N—N) are the differences between N—N bond distances of the second and third columns.

† The value calculated from the atomic coordinates given in reference (a) is 122.9°.

We thank BID-FINEP and FAPESP (Brazil) and CONICET and CIC Provincia Buenos Aires (Argentina) for financial support.

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Acta Cryst. (1982). **B38**, 2242–2245

Structure de l'Oxyde Double de Mercure et de Rhénium $Hg_5Re_2O_{10}$

PAR J.-P. PICARD, G. BAUD, J.-P. BESSE ET R. CHEVALIER

Equipe de Cristallographie et Physico-Chimie des Matériaux, ERA 897, Université de Clermont-Ferrand II, BP 45, 63170 Aubière, France

ET M. GASPÉRIN

Laboratoire de Minéralogie–Cristallographie, associé au CNRS, Université P. et M. Curie, 4 place Jussieu, 75230 Paris CEDEX 05, France

(Reçu le 19 janvier 1982, accepté le 22 mars 1982)

Abstract. $Hg_5Re_2O_{10}$, monoclinic, $P2_1/b$, $a = 6.401$ (5), $b = 7.981$ (5), $c = 11.538$ (7) Å, $\gamma = 98.87$ (19)° (from powder diagrams), $Z = 2$. Single-crystal diffraction data were collected on an automatic four-circle diffractometer. The structure has been refined by least-squares procedures to an R of 0.062 for 1791 observed reflexions. It can be visualized as composed of $(Hg_2)_4O_4$ rings formed by $(Hg_2)^{2+}$ pairs joined together by an O atom. These rings are bridged by Hg^{2+} atoms and form a two-dimensional network in which the ReO_4^- tetrahedra are located. The cohesion of this structure is assured by electrostatic bonds between $[(Hg_2)_4O_4Hg_2]_n^{4+}$ macrocations and ReO_4^- anions.

Introduction. Ce travail s'insère dans le cadre d'une étude cristalochimique des oxydes doubles $A-Re-O$ ($A =$ lanthanides, Y, alcalino-terreux, Cd, Hg, Pb) en vue d'en établir une éventuelle filiation structurale.

L'étude des systèmes $Ln-Re-O$ s'est révélée particulièrement riche et a permis de mettre en évidence des composés de structures très variées: $La_4Re_6O_{19}$ (Morrow & Katz, 1968; Longo & Sleight, 1968), $Nd_4Re_2O_{11}$ (Wilhelmi, Lagervall & Muller, 1970), Sm_3ReO_8 (Besse, Bolte, Baud & Chevalier, 1976), La_2ReO_5 (Waltersson, 1976), $La_6Re_4O_{18}$ (Besse, Baud, Chevalier & Gaspérin, 1978), La_3ReO_8 (Baud, Besse, Chevalier & Gaspérin, 1979), Y_3ReO_8 (Baud, Besse, Chevalier & Gaspérin, 1981). Par contre dans les