

Inorganic Chemistry

including bioinorganic chemistry

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Supporting Information

p1382

EXPERIMENTAL

Most of the important parameters for this project are condensed in Table 1. A yellow, parallelepiped-shaped single crystal of $(\text{Bu}_4\text{N})_2\text{Co}(\text{CN})_4 \cdot (\text{pyridine})$ (**2**), with approximate dimensions $0.36 \times 0.36 \times 0.42$ mm, was sealed in a capillary tube under nitrogen. The crystal was of modest quality and was found to diffract adequately in sharpness and intensity. Diffraction data was collected at 298°K using a Siemens P4 diffractometer in the range of $4.0^\circ \leq 2\theta \leq 45.0^\circ$ with $\text{MoK}\alpha$ radiation. A total of 3422 (3087 independent, $R_{\text{int}} < 0.01\%$) reflections were collected; of these 1334 had $F > 4.0\sigma(F)$. Photographic evidence showed *mmm* Laue symmetry and systematic absences in the diffraction data suggested either *Pbcm* or *Pbc2₁*. The former, centrosymmetric, alternative was suggested by the statistical distribution of *E*-values and by the potential presence of a mirror plane in the proposed structure. Refinement revealed that the potential crystallographic mirror plane coincides with that found in the structure, and all subsequent work was confined to the space group *Pbcm*. Therefore, the crystallographic asymmetric unit consists of one half of the anion and one whole cation. The plane passes perpendicularly through the plane of the pyridine ring.

The structure was solved by direct methods. The non-hydrogen atoms of the anion were refined with anisotropic displacement parameters; other displacement parameters were constrained to be isotropic. Hydrogen atom contributions were determined using a riding model with fixed isotropic *U* and a fixed bond length of 0.95Å. All computations were done using the Siemens SHELXTL PLUS (VMS) system.

DESCRIPTION OF STRUCTURE

A structural characterization was carried out on a yellow, parallelepiped-shaped crystal. Due to an inefficient packing arrangement (evidenced by the very low density and caused by weak inter-ionic forces), thermal activity in the lattice was high leading to a diffuse scatter of the radiation. The overall effect is an increase in the error limits for all reported measurements. However, the reliability of the reported structure is still extremely high and there can be no doubt that the reported structure is correct.

The unit-cell packing as viewed down the *a* axis (*b* is vertical and *c* is horizontal) is shown in Figure 5 in the body of the paper. The crystallographic mirror planes are perpendicular to the paper at 1/4 and 3/4 in *c*, as indicated by the arrows. It is immediately apparent that the anions stack in head-to-tail columns parallel to the *a* axis, and that these columns are completely surrounded by tubular columns of cations. The low density, due to a lack of strong inter-ionic forces, is clearly the result of packing these hydrophobic cationic columns like bundles of soda straws.

Given the packing arrangement, there are no significant inter-ionic contacts. The shortest $\text{Co}\cdots\text{Co}$ contact (9.024 Å) is along a column; the shortest inter-columnar $\text{Co}\cdots\text{Co}$ distance is 10.947 Å. The structure of the cation is as expected for a tetraalkylammonium ion.

The structure of the $[\text{pyCo}(\text{CN})_4]^{2-}$ ion is square pyramidal and is shown in Figure 4 in the body of the paper. Co is slightly elevated (0.183 Å) above the plane created by the carbon

atoms of the CN⁻ ligand. The sum of the angles around the basal plane is 357.9°. The pyridine ring is perpendicular to the base and offset slightly toward ligands 2 and 2a. The ring plane approximately bisects the C(1)-Co-C(2) angle. The slight asymmetry in the placement of the pyridine ring and the small difference in the two independent Co-C distances is probably the result of packing effects.