A Neutron-diffraction Study of $K_2Pb[Cu(NO_2)_6]$, an Example of a Regular Octahedral Copper(II) Complex

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CURRENT theory[1] forbids regular octahedral co-ordination for the copper(II) ion. To date, this has been supported by the structure determination of octahedrally co-ordinated copper(II) complexes with six identical ligands, *e.g.*, $[Cu(H_2O)_6](ClO_4)_2$, ($2 \times 2{\cdot}09$, $2 \times 2{\cdot}16$, $2 \times 2{\cdot}28$ Å);[2] $[Cu(H_2O)_6](NH_4)_2(SO_4)_2$, ($2 \times 2{\cdot}04$, $2 \times 2{\cdot}06$, $2 \times 2{\cdot}19$ Å);[3] ($2 \times 1{\cdot}961$, $2 \times 2{\cdot}095$, $2 \times 2{\cdot}219$ Å.[4] Recently, Bertrand and Carpenter[5] completed the structure of $K_2Ba[Co(NO_2)_6]$ in which the cobalt(II) ion is octahedrally co-ordinated to six nitrito-groups. It was felt that the related isomorphous copper(II) complex, $K_2Pb[Cu(NO_2)_6]$ would upset the accepted theory.

Previous *X*-ray structure determinations[6,7] of this compound used limited data, and because of the absorption of heavy atoms such as lead, copper, and potassium, there would be some

difficulty in determining accurately the positions of the light atoms. For these reasons, the structure was re-determined using neutron diffraction.

The green-black, cube octahedral crystals are cubic, $a = 10{\cdot}66 \pm 2$ Å, ($10{\cdot}68 \pm 2$ Å, X-ray[7]), $U = 1211$ Å^3, $Z = 4$, $D_m = 3{\cdot}43$, *space group*, $Fm3$ (T_h^3) or $F23$ (T^2); *atomic positions*: for space group $Fm3$: 8K in 8(*c*): $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$; 4Pb in 4(*b*): $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$; 4Cu in 4(*a*): 0,0,0; 24N in 24(*e*): 0·1984(4), 0,0; 48O in 48(*h*): 0, 0·0982(5), 0·2571(5). Isotropic temperature factors B: K, 3·9(4); Pb, 1·7(1); Cu, 1·4(1); N 2·5(1); O, 3·2(1) Å^2, μ (measured for neutrons) = 0·4 cm^{-1}; μ (X-ray, Cu-K_α) = 359 cm.$^{-1}$; μ (X-ray, Mo-K_α) = 163 cm.$^{-1}$.

The neutron-diffraction data was collected using the AINSE single-crystal and powder diffractometers installed on the Australian Atomic Energy Commission's reactor HIFAR at Lucas Heights, N.S.W. 195 independent reflections out of a possible 209 were collected up to $2\theta = 130°$ using a $2\theta/\theta$ step-scan technique. The spectrometer was monitor-controlled and the flux at the specimen was approximately 10^5n cm.^{2} sec.$^{-1}$, at a wavelength of 1·191 Å. Starting with Bertrand and Carpenter's[5] parameters for $K_2Ba[Co(NO_2)_6]$, the structure was refined using full-matrix least squares. Final $R = 0{\cdot}13$. The interatomic distances (Å) and angles are listed with those of previous studies in the Table.

The structure may be described as having a regular octahedral arrangement of the six nitrito-groups about the copper(II) ion. A distorted octahedron could be possible if the structure were disordered. However, this is discounted as no such signs were seen when a neutron powder-pattern was obtained by a 2θ scan, and the observed reflections examined. Elliot, Hathaway, and Slade[8] have suggested that the lack of distortion in the observed structure could be due to either a dynamic Jahn–Teller effect instantaneously producing four short and two long bonds, or a free rotation of the statically disordered NO_2^- groups in the lattice.

TABLE

Atoms	This work	Ref. 6	Ref. 7
Cu–N	2·11 (2)	2·24	2·03
N–O	1·22 (2)	1·15	1·38
Pb–O	2·79 (2)	2·87	2·72
K–O	3·12 (2)	3·10	3·13
Cu–O	2·93 (2)	—	—
∠O–N–O	118·2°	136°	108°

The isotropic B values in the present work are normal in character and three dimensional Fourier and difference-Fourier maps show that all the atoms are approximately spherical in nature. A notable exception is the nitrogen atom which suffers from some anisotropy concentrated along the axis away from the copper atom.

The structure is being refined using anisotropic temperature-factors and the complete structure will be published later.

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