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Thallium Lead Hexanitrocuprate(II) at 295 K

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Abstract. $\text{Tl}_2\text{PbCu}(\text{NO}_2)_6$, cubic, $Fm\bar{3}$, $a = 10.7344$ (5) Å at 295 K ($\lambda = 0.70926$ Å), $Z = 4$, $D_x = 5.131$ g cm $^{-3}$. It is isomorphous with $\text{K}_2\text{PbCu}(\text{NO}_2)_6$ at 295 K. The hexanitrocuprate(II) ion has $m\bar{3}$ symmetry with a Cu–N bond length of 2.118 (6) Å. The N–O bond distance is 1.252 (4) Å and the O–N–O angle is 116.6 (5)°.

Introduction. The greenish-black crystals of $\text{Tl}_2\text{PbCu}(\text{NO}_2)_6$ were grown by slow cooling (1°/h) of a saturated solution at 50° (Reinen, Friebel & Reetz, 1972). Laue symmetry, systematic absences (hkl with $h+k$, $k+l$, or $h+l$ odd) and the expected structure indicate the space group $Fm\bar{3}$.

The spherical data crystal was obtained by grinding in an abrasion chamber. The average diameter of the crystal was 0.1670 mm with a maximum of 0.1825 and a minimum of 0.1555 mm. The cell constants were determined from least-squares refinement of 2θ , ω , and χ values for 18 Mo $K\alpha_1$ reflections measured at 2θ angles of about 47°.

A four-circle automated diffractometer was used to collect intensity data at 295 K for 3143 reflections out to $2\theta = 90^\circ$ (Nb-filtered Mo $K\alpha$ radiation $12^\circ < 2\theta < 90^\circ$ and Zr–Y balanced filters $0^\circ < 2\theta < 12^\circ$). The 2θ step

scan mode provided in the diffractometer control program (Lenhert, 1975) was used. The 2θ scan range included the usual constant factor and the 2θ dependent dispersion factor; the number of steps was adjusted automatically so that 25 steps per degree were used for all reflections. 2825 reflections from the hkl and $-h, -k, -l$ octants were measured with 4 s step counts and two 40 s background measurements at the limits of the 2θ scan. In order to reduce the influence of unobserved reflections on the refined parameters and on the electron density map an additional 318 weak reflections were remeasured in other octants with 10 s step counts and 100 s background measurements. All observations were averaged to give 479 symmetry independent reflections with only 4 unobserved ($F_o = 0$). Monitor reflections showed an intensity decrease of 1% at the end of 270 hours of X-ray exposure.

Absorption corrections for the spherical crystal were based on published tables (Weber, 1969). A^* values were interpolated for $\mu R = 3.38$ and $1/A^*$ was fitted to a 7th order polynomial in $\sin^2 \theta$. \bar{T} values for extinction corrections (Zachariasen, 1968) were approximated by a similar 7th order polynomial. Both fits gave maximum errors of 0.5% or less in the range

Table 1. *Positional and thermal parameters for $\text{Tl}_2\text{PbCu}(\text{NO}_2)_6$*

The thermal parameters are of the form

$$T = \exp \left[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*) \right]$$

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	0	0	0	1.35 (2)					
Pb	0	0	$\frac{1}{2}$	1.47 (1)					
Tl	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	2.95 (1)					
O	0.09922 (31)	0	0.25861 (31)	2.01 (12)	3.21 (15)	3.38 (16)	0	-0.38 (12)	0
N	0	0	0.19727 (53)	2.26 (19)	1.75 (17)	2.61 (22)			

of interest ($2\theta < 90^\circ$). Further details of the data collection and reduction methods have been described previously (Miller, Lenhert & Joesten, 1972).

The crystal structure of $\text{Tl}_2\text{PbCu}(\text{NO}_2)_6$ was refined, taking as starting parameters those obtained for the isostructural $\text{K}_2\text{PbCu}(\text{NO}_2)_6$ (Cullen & Lingafelter, 1971). Weights for the full-matrix least-squares refinement were based on counting statistics and included an instability term with a value of 1.1%. The isotropic extinction parameter, r^* (Zachariasen, 1968), refined to 0.04717×10^{-4} cm. The final cycle included unobserved reflections and gave a shift-to-error ratio of 0.6 for the largest parameter shift; a conventional R of 0.036, and a weighted residual, $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$, of 0.022. The final difference map showed a maximum $\Delta\rho$ of $3.0 \text{ e } \text{\AA}^{-3}$ at the Pb position and a minimum $\Delta\rho$ of $-1.3 \text{ e } \text{\AA}^{-3}$ near each of the Cu, Pb, and Tl atoms. Other details of the refinement procedure are described in Takagi, Joesten & Lenhert (1975a). The final parameters are reported in Table 1.*

Discussion. The $\text{Tl}_2\text{PbCu}(\text{NO}_2)_6$ structure reported here (Fig. 1) was selected for study to allow comparison with $\text{K}_2\text{PbCu}(\text{NO}_2)_6$, the first reported case of octahedral symmetry for Cu (II) (see Cullen & Lingafelter, 1971; and references therein). Previous e.p.r. and X-ray studies (Reinen *et al.*, 1972; Harrowfield, Dempster, Freeman & Pilbrow, 1973; Harrowfield & Pilbrow, 1973) indicate both compounds undergo phase transitions to lower symmetry lattices when the temperature is reduced. Single crystal X-ray diffraction studies in our laboratory indicate that members of the

$\text{M}_2\text{M}'\text{Cu}(\text{NO}_2)_6$ series are either cubic ($Fm\bar{3}$) or orthorhombic ($Fmmm$) at 295 K. The CuN_6 configuration in the lower symmetry orthorhombic crystals (compressed or elongated) depends on the counter ions. We have previously reported the structure of $\text{K}_2\text{CaCu}(\text{NO}_2)_6$, $\text{K}_2\text{BaCu}(\text{NO}_2)_6$, and $\text{Rb}_2\text{PbCu}(\text{NO}_2)_6$ which illustrate this point (Takagi, Lenhert & Joesten, 1974; Takagi, Joesten & Lenhert, 1975a, b, c).

The present study confirms the cubic structure of $\text{Tl}_2\text{PbCu}(\text{NO}_2)_6$ at 295 K. Bond distances, bond angles and r.m.s. displacements of N atoms for $\text{Tl}_2\text{PbCu}(\text{NO}_2)_6$ are compared with those of $\text{K}_2\text{PbCu}(\text{NO}_2)_6$ in Table 2. The results for $\text{Tl}_2\text{PbCu}(\text{NO}_2)_6$ are essentially identical with those of $\text{K}_2\text{PbCu}(\text{NO}_2)_6$. The N atoms show greater thermal motion along the Cu-N bond than at right angles to it, although the difference between U_{11} and U_{33} for the $\text{Tl}_2\text{PbCu}(\text{NO}_2)_6$ crystals is, statistically, only suggestive because of the larger errors. This

Table 2. Interatomic distances and angles and r.m.s. nitrogen atom displacements for $\text{Tl}_2\text{PbCu}(\text{NO}_2)_6$ and $\text{K}_2\text{PbCu}(\text{NO}_2)_6$ at 295 K

	$\text{Tl}_2\text{PbCu}(\text{NO}_2)_6^{(a)}$	$\text{K}_2\text{PbCu}(\text{NO}_2)_6^{(b)}$
Cu-N	2.118 (6) Å	2.118 (2) Å
Pb-O	2.802 (3)	2.778 (1)
Tl-O	3.135 (2)	K-O 3.116 (1)
N-O	1.252 (4)	1.247 (2)
O-N-O	116.6 (5)°	116.9 (2)°
U_{11}	0.169 (7) Å ²	0.170 (2) Å ²
U_{22}	0.149 (7)	0.164 (2)
$U_{33}^{(c)}$	0.182 (8)	0.182 (2)

(a) This work. (b) Takagi, Joesten, Lenhert (1975d). (c) U_{33} is the N atom r.m.s. displacement in Å along the Cu-N bond.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31374 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

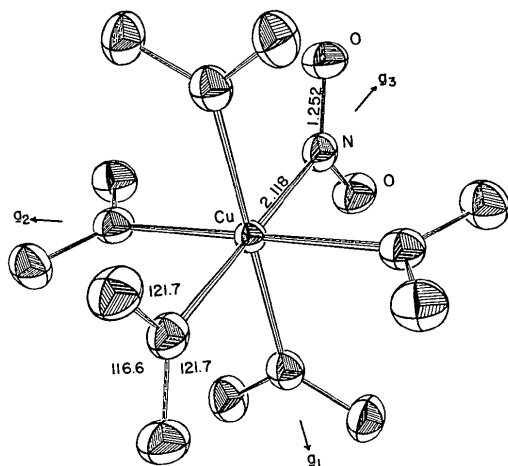


Fig. 1. Hexanitrocuprate(II) anion with bond distances and angles and atomic numbering. Thermal ellipsoids drawn at 50% probability by ORTEP (Johnson, 1965).

feature of the thermal motion has been interpreted as support for the presence of a dynamic Jahn-Teller effect (Cullen & Lingafelter, 1971).

The effect which different counter ions have on the dynamic-static distortions of $\text{Cu}(\text{NO}_2)_4^{2-}$ is still not explained but it is evidently related to the size of the monovalent counter ion. Rb^+ , Tl^+ and K^+ in $\text{M}_2\text{PbCu}(\text{NO}_2)_6$ have cubic to orthorhombic transitions at 44, 18, and 8° respectively (Takagi, Joesten & Lenhert, 1975c; Harrowfield *et al.*, 1973; Harrowfield & Pilbrow, 1973). This correlates with the difference between the observed M-O distances and the sum of the ionic radii for the 3 ions. Rb^+ (radius, 1.48 Å) with a Rb-O distance of 3.147 Å (Takagi *et al.*, 1975b) is nearly in contact with its neighboring O atoms. At the other end of the scale, K^+ (radius, 1.33 Å) with a K-O distance of 3.116 Å is a very loose fit in the 'pocket' formed by the $\text{Cu}(\text{NO}_2)_4^{2-}$ groups (see illustration and discussion in Takagi, Joesten & Lenhert, 1975e). Tl^+ (radius, 1.44 Å) is intermediate with an intermediate transition temperature. These observations suggest that the looser packing allows the static-to-dynamic transition to take place at a lower temperature.

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3,4-Benzopyrene (A New Refinement)

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Abstract. $C_{20}H_{12}$, monoclinic, $P2_1/c$, $a=4.535$ (5), $b=20.40$ (2), $c=13.49$ (1) Å, $\beta=97.0^\circ$, $D_m=1.351$, $Z=4$, $D_x=1.351$ g cm $^{-3}$. The structure determined by Iball & Young (1956) has been refined to an R of 0.069 for 1165 observed reflexions. The molecule is almost planar (deviations less than ± 0.04 Å) and, as expected,

has two short bonds (1.342 and 1.352 Å) in the 'K regions' of the two phenanthrene nuclei.

Introduction. The structure of the monoclinic form of 3,4-benzopyrene was described by Iball & Young (1956) but since the coordinates were based mainly on

Table 1. *Final atomic coordinates ($\times 10^4$) and temperature factors ($\times 10^4$) (e.s.d.'s in parentheses)*

$$T = \exp [-(h^2b_{11} + k^2b_{22} + l^2b_{33} + hkb_{12} + klb_{23} + hlb_{13})].$$

	x	y	z	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
C(1)	1172 (20)	-747 (4)	962 (6)	601 (51)	31 (19)	11 (28)	24 (2)	0 (6)	49 (5)
C(2)	-823 (19)	-1231 (4)	719 (6)	553 (50)	46 (20)	17 (28)	28 (3)	-1 (6)	46 (5)
C(3)	-1597 (18)	-1691 (4)	1456 (6)	461 (44)	35 (18)	44 (26)	23 (2)	-18 (6)	58 (5)
C(4)	-3687 (20)	-2198 (5)	1223 (7)	533 (51)	26 (21)	26 (31)	30 (3)	-35 (7)	75 (6)
C(5)	-4338 (22)	-2622 (5)	1959 (7)	729 (60)	-59 (23)	111 (34)	30 (3)	-11 (8)	77 (7)
C(6)	-2939 (21)	-2577 (4)	2922 (7)	629 (53)	-4 (21)	135 (31)	24 (2)	-6 (7)	83 (6)
C(7)	-857 (19)	-2078 (4)	3172 (6)	534 (46)	33 (19)	111 (26)	24 (2)	3 (6)	60 (5)
C(8)	619 (21)	-2013 (5)	4169 (7)	688 (56)	54 (22)	102 (31)	28 (3)	12 (7)	64 (6)
C(9)	2603 (20)	-1535 (5)	4419 (6)	666 (54)	61 (21)	38 (29)	29 (3)	12 (7)	49 (5)
C(10)	3357 (19)	-1063 (4)	3690 (6)	462 (45)	48 (18)	26 (26)	26 (2)	-1 (6)	48 (5)
C(11)	5359 (19)	-575 (4)	3936 (6)	518 (49)	44 (20)	-24 (29)	28 (3)	-8 (7)	56 (5)
C(12)	6078 (19)	-113 (4)	3217 (7)	512 (48)	27 (19)	54 (29)	21 (2)	-7 (6)	67 (6)
C(13)	8156 (21)	398 (5)	3496 (7)	550 (51)	39 (21)	36 (32)	28 (3)	-19 (7)	78 (6)
C(14)	8876 (22)	853 (5)	2814 (8)	649 (55)	-10 (23)	114 (34)	28 (3)	-19 (8)	95 (7)
C(15)	7478 (22)	817 (5)	1834 (7)	733 (57)	-9 (22)	181 (33)	23 (2)	-5 (8)	92 (7)
C(16)	5460 (21)	337 (4)	1548 (7)	666 (53)	52 (21)	147 (29)	26 (2)	1 (7)	65 (6)
C(17)	4686 (19)	-148 (4)	2225 (6)	529 (46)	47 (18)	73 (26)	23 (2)	0 (6)	51 (5)
C(18)	2603 (18)	-666 (4)	1953 (6)	484 (45)	38 (18)	23 (25)	23 (2)	0 (6)	48 (5)
C(19)	1930 (18)	-1112 (4)	2676 (6)	448 (43)	53 (16)	19 (24)	24 (2)	-1 (6)	38 (4)
C(20)	-157 (18)	-1624 (4)	2444 (6)	445 (39)	47 (17)	66 (23)	22 (2)	2 (6)	48 (4)