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Potassium Strontium Hexanitrocuprate(II) and Potassium Strontium Hexanitronickelate(II)

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Abstract. The $K_2SrCu(NO_2)_6$ crystals are orthorhombic, *Fmmm*; $a=10{\cdot}4301$ (7), $b=10{\cdot}4621$ (7), $c=10{\cdot}9368$ (9) Å; $\lambda=0{\cdot}70926$ Å; 295K; $Z=4$, $D_x=2{\cdot}813$, $D_m=2{\cdot}814$ g cm^{-3}. The $K_2SrNi(NO_2)_6$ crystals are cubic, *Fm*3; $a=10{\cdot}5063$ (5) Å; $\lambda=1{\cdot}54051$ Å; 295K; $Z=4$, $D_x=2{\cdot}867$, $D_m=2{\cdot}863$ g cm^{-3}. The hexanitrocuprate(II) ion is elongated along one axis to give Cu–N distances of 2·310 (2), 2·041 (2) and 2·029 (2) Å but the non-Jahn–Teller Ni complex has equal Ni–N distances of 2·078 (1) Å.

Introduction. Crystals of $K_2SrCu(NO_2)_6$ and $K_2SrNi(NO_2)_6$ were obtained by slow cooling (1° h^{-1}) of a saturated solution at 50°C (Reinen, Friebel & Reetz, 1972). Data for the two crystals are given in Table 1. Both the orthorhombic *Fmmm* and cubic *Fm*3 space groups have the same systematic absences (*hkl* with $h+k$, $k+l$ or $h+l$ odd). The appropriate space group for each compound is indicated by the Laue symmetry and confirmed by the successful refinement. Intensity data were measured at 295K on a computer-controlled four-circle diffractometer with programs described by Lenhert (1975). Details of the procedures used for data collection, data reduction and structure refinement have been published previously (Miller, Lenhert & Joesten, 1972). Pertinent information about the data and refinement parameters for both $K_2SrCu(NO_2)_6$ and $K_2SrNi(NO_2)_6$ are listed in Table 1 and are given in the following discussion.

$K_2SrCu(NO_2)_6$. The cell constants were determined from the least-squares refinement of 2θ, ω and χ values for 18 Mo $K\alpha_1$ ($\lambda=0{\cdot}70926$ Å) reflections ($62<2\theta<66°$). Intensity data were collected with Nb-filtered Mo $K\alpha$ radiation, θ–2θ scans at 1° min^{-1} and a total background count of 80 s. An additional 562 weak reflections were remeasured with unfiltered Mo $K\alpha$ radiation, θ–2θ scans at 0·5° min^{-1} and a total background count of 200 s. The structure was refined by full-matrix least-squares calculations using as starting parameters those obtained for isostructural $K_2BaCu(NO_2)_6$ (Takagi, Joesten & Lenhert, 1975*b*). $\sum w(|F_o|-|F_c|)^2$ was minimized, where $w=1/\sigma^2(F)$; σ

Table 1. *Crystal and refinement data*

	$K_2SrCu(NO_2)_6$	$K_2SrNi(NO_2)_6$
Color	Green	Brown-yellow
Crystal size	0·14 × 0·16 × 0·20 mm	0·07 × 0·13 × 0·15 mm
Crystal volume	0·0042 mm^3	0·0015 mm^3
Number of reflections		
Total measured	3451 ($h,k,\pm l$)	2828 ($h,k,\pm l$)
Averaged	1377 (34 with $F_o<0$)	453 (3 with $F_o<0$)
X-ray exposure time	249 h	199 h
Intensity decrease	9 %	2 %
X-ray intensity fluctuation	0·565 %	1·244 %
Absorption corrections		
Linear absorption coeff.	68·7 cm^{-1}	68·5 cm^{-1}
Gaussian integration grid	10 × 10 × 10	10 × 10 × 10
Max. transmission factor	0·447	0·610
Min. transmission factor	0·359	0·408
Final refinement cycle		
Ave. shift/error	0·014	0·042
Max. shift/error	0·065	0·270
R (all reflexions)	0·031	0·026
$R_w=[\sum w(\lvert F_o\rvert-\lvert F_c\rvert)^2/\sum w\lvert F_o\rvert^2]^{1/2}$	0·019	0·018
S.E. of an observation	2·41	2·19
Final difference map		
Max. $\Delta\varrho$	1·8 at Cu	1·3 at Ni
Min. $\Delta\varrho$	−0·8 near Cu	−0·9 near Ni
Extinction parameter (r^*)	0·3611 × 10^{-4} cm	0·0889 × 10^{-4} cm

includes the instability factor from Table 1 as well as the usual counting statistics. All atoms were refined anisotropically along with an isotropic extinction parameter (Zachariasen, 1968). Atomic scattering factors (for neutral atoms) were those tabulated by Cromer & Mann (1968). Anomalous scattering factors (used for Sr, Cu and K) were those of Cromer & Liberman (1970). Computer programs have been referenced previously (Takagi *et al.*, 1975*b*). The final positional and thermal parameters are given in Table 2.*

$K_2SrNi(NO_2)_6$. The cell constants were determined as described above with Ni-filtered Cu $K\alpha_1$ radiation ($\lambda = 1{\cdot}54051$ Å). Intensity data were collected with Nb-filtered Mo $K\alpha$ radiation, as above with 126 weak reflections rescanned at the slower speed. The structure was refined using as starting parameters those obtained for the isostructural $K_2PbNi(NO_2)_6$ (Takagi, Joesten & Lenhert, 1975*c*). Refinement methods, computer programs and form factors are described or referenced above. Pertinent refinement parameters are given in Table 1 and the final positional and thermal parameters are given in Table 2.

Discussion. The $Cu(NO_2)_6^{4-}$ cluster is ideal for studies of the dynamic–static Jahn–Teller effect. X-ray diffraction studies indicate that the CuN_6 configuration has $m3$ symmetry in the cubic crystals of $K_2PbCu(NO_2)_6$ (Cullen & Lingafelter, 1971) and $Tl_2PbCu(NO_2)_6$ (Takagi, Joesten & Lenhert, 1976*a*). However, both compounds undergo a phase transition at reduced temperature to an orthorhombic form which shows a compressed tetragonal configuration for the CuN_6 group (Joesten; Takagi & Lenhert, 1976; Harrowfield & Pilbrow, 1973; Harrowfield, Dempster, Freeman & Pilbrow, 1973). Other compounds in the $M_2M'Cu(NO_2)_6$ series are orthorhombic at 295K with a compressed tetragonal configuration for CuN_6 when M = Rb and M′ = Pb (Takagi, Joesten & Lenhert, 1975*a*, 1976*c*) and an elongated tetragonal configuration when M = K and M′ = Ca, Ba (Takagi, Lenhert & Joesten, 1974; Takagi *et al.*, 1975*b*). Structures of several corresponding Ni^{II} complexes, all of which are cubic, have been determined (Takagi *et al.*, 1975*c*; Takagi, Joesten & Lenhert, 1975*d*).* The present paper reports the structures of $K_2SrCu(NO_2)_6$ and $K_2SrNi(NO_2)_6$ which are of interest as a further comparison of the Jahn–Teller Cu^{II} ion and the non-Jahn–Teller Ni^{II} and as an extension of both the $M_2M'Cu(NO_2)_6$ and $M_2M'Ni(NO_2)_6$ series to include Sr^{2+}, an ion about the size of Pb^{2+} and intermediate in size between Ca^{2+} and Ba^{2+}.

$K_2SrCu(NO_2)_6$. A comparison of the $Cu(NO_2)_6^{4-}$ distances and angles given in Table 3 with those found for the Ca and Ba crystals (Takagi *et al.*, 1975*b*, Table 2) again confirms that a change from one alkaline-earth counter ion to another has little effect on the $Cu(NO_2)_6^{4-}$ geometry. Comparison also confirms our earlier observation that the O–N–O angle is smaller by about 1° and the N–O distance larger by about 0·006 Å for the distant NO_2 groups of the cluster as compared with the closer NO_2 groups. A more detailed discussion of these observations will be given in a later paper (Joesten *et al.*, 1976).

$K_2SrNi(NO_2)_6$. A comparison of the $Ni(NO_2)_6^{4-}$ geometry given in Table 3 with that found for the Ba^{2+} and Pb^{2+} crystals (Takagi *et al.*, 1975*c*, Table 2; Takagi *et al.*, 1975*d*, Table 3) shows identical distances and angles except for the O–N–O angle which is 1° smaller

Table 2. *Positional and thermal parameters for* $K_2SrCu(NO_2)_6$ *and* $K_2SrNi(NO_2)_6$

The thermal parameters are of the form $T = \exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

	x/a	y/b	z/c	B_{11} or B	B_{11}	B_{22}	B_{12}	B_{13}	B_{23}
$K_2SrCu(NO_2)_6$									
Cu	0	0	0	0·786 (11)	0·843 (11)	1·179 (12)			
Sr	0	0	$\frac{1}{2}$	0·867 (9)	0·865 (9)	0·945 (9)			
K	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	2·582 (19)	2·503 (18)	2·847 (20)			
O(1)	0	0·10130 (9)	0·27200 (8)	3·31 (5)	1·36 (3)	1·46 (4)	0	0	−0·14 (3)
O(2)	0·10160 (9)	0·25710 (10)	0	1·36 (3)	1·31 (3)	3·35 (5)	−0·29 (3)	0	0
O(3)	0·25726 (10)	0	0·09698 (9)	1·40 (3)	2·84 (4)	1·62 (3)	0	−0·34 (4)	0
N(1)	0	0	0·21118 (15)	1·58 (6)	1·63 (6)	1·11 (5)			
N(2)	0	0·19509 (15)	0	1·33 (5)	0·97 (5)	1·31 (5)			
N(3)	0·19456 (15)	0	0	1·01 (5)	1·16 (5)	1·51 (6)			
$K_2SrNi(NO_2)_6$									
Ni	0	0	0	0·782 (8)					
Sr	0	0	$\frac{1}{2}$	0·777 (7)					
K	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	2·258 (11)					
O	0	0·10098 (7)	0·26042 (9)	2·69 (3)	1·26 (3)	1·20 (3)	0	0	−0·29 (2)
N	0	0	0·19778 (13)	1·13 (4)	1·17 (4)	0·96 (4)	0	0	0

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* A list of structure factors for both compounds has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31755 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

* In Takagi *et al.* (1975*c*,*d*) two figures have been transposed in printing (see Takagi, Joesten & Lenhert, 1976*b*).

Table 3. *Bond distances* (Å) *and angles* (°)

	$K_2SrCu(NO_2)_6$	$K_2SrNi(NO_2)_6$
Cu(Ni)–N(1)	2·310 (2)	2·078 (1)
Cu——N(2)	2·041 (2)	–
Cu——N(3)	2·029 (2)	–
N(1)—O(1)	1·251 (1)	1·248 (1)
N(2)—O(2)	1·242 (1)	–
N(3)—O(3)	1·246 (1)	–
Sr———O(1)	2·709 (1)	2·732 (1)
Sr———O(2)	2·753 (1)	–
Sr———O(3)	2·745 (1)	–
K———O(1)	3·046 (1)	3·060 (1)
K———O(2)	3·143 (1)	–
K———O(3)	3·106 (1)	–
O(1)–N(1)–O(1)	115·8 (1)	116·4 (1)
O(2)–N(2)–O(2)	117·1 (1)	–
O(3)–N(3)–O(3)	116·7 (1)	–

in $K_2SrNi(NO_2)_6$. No evidence of the NO_2 disorder noted in $K_2BaNi(NO_2)_6$ crystals is found in the present case. We have observed (Takagi *et al.*, 1975*d*) that the disorder was present in the $M_2M'Ni(NO_2)_6$ crystals with the large M′ counter ion (Ba^{2+}, radius 1·35 Å) and was absent in crystals with the smaller ion (Pb^{2+}, radius 1·21 Å). The present case (Sr^{2+}, radius 1·13 Å) supports our earlier conjecture that ion size rather than bonding properties (Pb^{2+} *vs* Ba^{2+}) is the determining factor in allowing or preventing NO_2 group disorder.

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2-(Isopropylideneaminooxy)propion-*p*-bromoanilide

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Abstract. $C_{12}H_{15}N_2O_2Br$, monoclinic, $P2_1$, $a=12\cdot979$ (5), $b=10\cdot411$ (6), $c=10\cdot138$ (4) Å, $\beta=96\cdot95$ (4)°, $M=299\cdot2$, $Z=4$, $D_x=1\cdot46$ g cm^{-3}. The unit cell contains two independent molecules which do not differ significantly in their geometrical parameters; both exhibit the *S* configuration. By chemical correlation this configuration is thereby also confirmed for 2-(2,4,5,7-tetranitro-9-fluorenylideneaminooxy)propionic acid (TAPA), a valuable reagent for the resolution of racemic Lewis bases.

Introduction. Cell dimensions were determined by a least-squares fit to the settings for 15 reflexions ($\pm hkl$) on a Syntex $P2_1$ four-circle diffractometer (Mo $K\alpha$, 0·71069 Å). Intensities from a prismatic crystal, $0\cdot18\times0\cdot22\times0\cdot42$ mm, were collected on the diffractometer with graphite-monochromated Mo $K\alpha$ radiation. Measurements were carried out in the θ–2θ mode ($3\cdot0\le2\theta\le50\cdot0°$) at scan speeds varying linearly between 2·93° min^{-1} (150 c.p.s. and below) and 29·3° min^{-1} (5000 c.p.s. and above). Scan and background