

molybdenum oxides, while even stronger Mo—Mo bondings such as the triple bond (Chisholm, Cotton, Extine & Murillo, 1978) and the quadruple bond (Cotton, Extine & Gage, 1978) have been known in some non-oxide compounds. The Mo—Mo bonding concerned forms the triangular atom groups of Mo_3O_{13} in the MoO_6 layer (Fig. 1). Such a group was termed 'metal-atom cluster' and the strong metal-to-metal bonding was already established for Mo_3O_{13} using the LCAO—MO calculation by Cotton (1964). The short Mo—Mo bond may have caused the variation in the Mo—O distance which ranges from 1.953 to 2.135 Å, giving distorted MoO_6 octahedra. On the other hand, Fe—O distances in both FeO_4 and FeO_6 polyhedra are found to be normal (Shannon & Prewitt, 1969).

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Structure of Barium Dipotassium Hexanitrocobaltate(II): a Redetermination

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Abstract. $\text{BaK}_2[\text{Co}(\text{NO}_2)_6]$, $M_r = 550.5$, cubic, $Fm\bar{3}$, $a = 10.653(2)$ Å, $V = 1209.0$ Å³, $Z = 4$, $D_x = 3.024$ g cm⁻³, $\text{Mo } K\alpha$, $\lambda = 0.71069$ Å, $\mu = 53.45$ cm⁻¹, $F(000) = 1036$, $T = 294$ K, final $R = 0.027$ for 323 reflections. The $[\text{Co}(\text{NO}_2)_6]^{4-}$ anion has $m\bar{3}$ (T_h) symmetry. The Co—N distance is 2.010(3) Å, which is only 0.06 Å longer than in an analogous Co^{III} complex. The thermal ellipsoid of the N atom reveals no anisotropy, in contrast with other structures containing the same complex anion.

Introduction. Low-spin octahedral complexes of d^7 ions are expected to be distorted by a Jahn–Teller effect. However, compounds of the type $M^{\text{II}}M^{\text{I}}_2[\text{Co}(\text{NO}_2)_6]$ are cubic with all Co—N distances equal (Lenhert & Joesten, 1980; Bertrand & Carpenter, 1966). It is possible that the octahedral symmetry is the result of a dynamic rather than static Jahn–Teller effect.

The structure of $\text{BaK}_2[\text{Co}(\text{NO}_2)_6]$ has been determined twice previously: at room temperature where octahedral symmetry about Co was observed (Bertrand & Carpenter, 1966) and at 233 K where three different Co—N distances were observed (Bertrand, Carpenter & Kalyanaraman, 1971). In both cases the structures

were determined from film data and hence were of limited precision. Recent, precise determinations of the structures of $\text{PbK}_2[\text{Co}(\text{NO}_2)_6]$ and $\text{PbRb}_2[\text{Co}(\text{NO}_2)_6]$ (Lenhert & Joesten, 1980) have revealed anisotropic thermal parameters suggestive of a dynamic Jahn–Teller effect. In order to establish whether such an effect is also evident in the title compound, and to obtain more precise bond lengths for comparison with the aforementioned compounds, we have redetermined its structure using counter-measured data.

Experimental. Data collected using Enraf–Nonius CAD-4 automatic diffractometer, graphite-monochromated $\text{Mo } K\alpha$ radiation; 18 independent reflections with $20^\circ \leq 2\theta \leq 65^\circ$ used for least-squares determination of cell constant. Intensities of three reflections monitored, less than 1% decomposition. Full-matrix least-squares refinement based on F values, starting from previously published coordinates (Bertrand & Carpenter, 1966), converged with all shifts less than 0.001σ . Max. excursions in final difference map 0.8 and -1.1 e Å⁻³. All calculations performed with *SHELX76* (Sheldrick, 1976). Scattering factors and anomalous-dispersion terms taken from *International*

Tables for X-ray Crystallography (1974). Data-collection and refinement parameters are collected in Table 1. Final positional and thermal parameters are listed in Table 2.† A view of the complex anion is shown in Fig. 1 and a stereoview of the unit cell in Fig. 2. Figures were drawn with *ORTEP* (Johnson, 1965).

Discussion. The present determination of the structure of $\text{BaK}_2[\text{Co}(\text{NO}_2)_6]$ confirms the results of the previous study but provides bond distances an order of magnitude more precise. Bond lengths and angles are compared with those of related structures in Table 3. The Co—N distance is the shortest of those observed. It has been suggested that the Co—N distance is affected by the size of the M^+ and M^{2+} cations (Lenhert & Joesten, 1980). Thus, in the $\text{PbRb}_2[\text{Co}(\text{NO}_2)_6]$ structure, the relatively large Rb^+ cation causes an expansion of the lattice and a longer Co—N bond results while in $\text{PbK}_2[\text{Co}(\text{NO}_2)_6]$ the smaller K^+ cation fits loosely in the lattice and a smaller Co—N distance results (Lenhert & Joesten, 1980). In the $\text{BaK}_2[\text{Co}(\text{NO}_2)_6]$ structure the larger Ba^{2+} cation causes tight packing along the cell axis and so the Co—N bond is compressed. The K^+ cation is consequently only loosely packed as is confirmed by the K—O distance and the high thermal parameter of this atom.

It was also noted previously that the strength of the contacts $\text{Co—NO}_2\text{—}M^{2+}$ apparently affects the thermal motion of the N atom. Where the contact is 'loose' large anisotropy in the direction of the Co—N bond is observed and as the contact tightens the anisotropy decreases (Lenhert & Joesten, 1980). This trend is confirmed in the present structure; the contact is tightly compressed and there is essentially no anisotropy in the thermal ellipsoid of the N atom. Evidently the compression of the Co—N bond is associated with a damping of the motion in the direction of this bond. It seems likely that this motion is a consequence of a dynamic Jahn—Teller effect in which case we must conclude that this effect can be altered by crystal-packing forces.

A second point of interest is the comparison of the length of the Co^{II} —ligand bond with that in an analogous Co^{III} complex. A precise determination of the structure of $\text{K}_2\text{Na}[\text{Co}(\text{NO}_2)_6]$ gives a Co^{III} —N distance of 1.9516 (7) Å (Ohba, Toriumi, Sato & Saito, 1978). This is 0.06 Å shorter than the distance of 2.010 (3) Å found in the present study and 0.09 Å shorter than the longest Co^{II} —N distance found in the $\text{PbRb}_2[\text{Co}(\text{NO}_2)_6]$ structure (Lenhert & Joesten, 1980). This difference of 0.06–0.09 Å corresponds to the introduction of one σ -antibonding e_g^* electron to the

† Lists of structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42475 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Summary of data-collection and processing parameters

Crystal dimensions	0.30 × 0.09 × 0.09 mm
Data-collection range	$2^\circ < 2\theta < 150^\circ$
Scan width	$(2.10 + 0.35 \tan\theta)^\circ$
Horizontal counter aperture	$(2.00 + 0.50 \tan\theta)$ mm
Scan type	ω
Absorption correction:	
number of sampling points	16 × 6 × 6
max. correction	2.382
min. correction	1.491
Range of hkl	0–24
Total data collected	702
Unique data after merging	530
R_{int}	0.011
Data with $I > 2.5\sigma(I)$	323
Total variables	15
R	0.027
wR	0.033
Weighting constants	$g = 1.0, k = 0.0005$
$[w = g/(\sigma^2 F_o + kF_o^2)]$	

Table 2. Fractional coordinates ($\times 10^4$) and thermal parameters ($\text{Å}^2 \times 10^4$)

	x	y	z	U
Co	0	0	0	175 (1)
O	0	2504 (2)	998 (2)	
N	0	1887 (3)	0	
Ba	0	5000	0	221 (1)
K	2500	2500	2500	450 (4)
	U_{11}	U_{22}	U_{33}	U_{23}
O	591 (17)	299 (9)	255 (7)	−44 (7)
N	260 (11)	278 (11)	228 (11)	

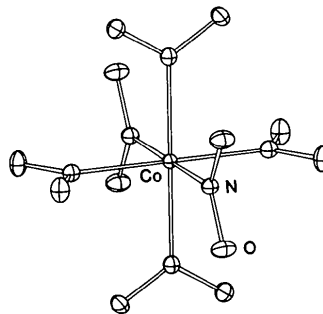


Fig. 1. The $[\text{Co}(\text{NO}_2)_6]^{4-}$ anion with atom labelling. Thermal ellipsoids are drawn at the 50% probability level.

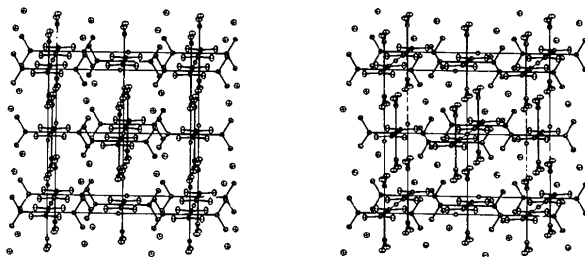


Fig. 2. Stereoview of the unit cell. Ba^{2+} ions are shown as small spheres along the cell edges and at the centre of the cell, K^+ as larger spheres at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ etc.

Table 3. *Interatomic distances (Å) and angles (°) for complexes of the type $MM_2[Co(NO_2)_6]$*

	BaK ₂ [Co(NO ₂) ₆]	PbK ₂ [Co(NO ₂) ₆]	PbRb ₂ [Co(NO ₂) ₆]
Co—N	2.010 (3)	2.024 (3)	2.046 (3)
N—O	1.250 (3)	1.236 (4)	1.243 (2)
Ba—O or Pb—O	2.864 (2)	2.782 (3)	2.814 (2)
K—O or Rb—O	3.107 (2)	3.054 (2)	3.096 (1)
O—N—O	116.6 (3)	117.2 (4)	116.7 (1)
Co—N—O	121.7 (2)	121.4 (2)	121.7 (1)

Co^{III} (t_{2g})⁶ electron configuration to give the low-spin Co^{II} (t_{2g})⁶(e_g^*)¹ configuration. In contrast, a difference as large as 0.21 Å occurs between low-spin (t_{2g})⁶ Co(H₂O)₆³⁺ and high-spin (t_{2g})⁵(e_g^*)² Co(H₂O)₆²⁺ (Beattie, Best, Skelton & White, 1981).

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Decaselenium Bis(fluorosulfate)

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Abstract. Se₁₀[SO₃F]₂, $M_r = 987.7$, orthorhombic, $P2_12_12_1$, $a = 8.627$ (1), $b = 13.114$ (3), $c = 15.135$ (3) Å, $U = 1712.3$ (6) Å³, $Z = 4$, $D_x = 3.83$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 23.19$ mm⁻¹, $F(000) = 1752$, $T = 295$ K, $R = 0.0749$ for 1779 observed reflections. The structure contains Se₁₀²⁺ cations (of the bicyclo[4.2.2]decane type) and fluorosulfate anions. Se—Se bond lengths in the cation vary in length from 2.246 (5) to 2.450 (5) Å.

Introduction. S, Se and Te can be oxidized under suitable conditions to polyatomic cations such as S₈²⁺, Se₁₀²⁺ and Te₄²⁺ (Gillespie, 1979). The structures of several of these cations in the solid state have been determined (Gillespie, 1979). In order to determine if these structures are maintained in solution ⁷⁷Se and ¹²⁵Te NMR studies have been carried out (Burns, Granger & Schrobilgen, 1978; Lassigne & Wells, 1978). During a continuation of these studies the precipitate obtained from the reaction of equimolar amounts of selenium, tellurium and arsenic pentafluoride in SO₂ solution was dissolved in 30% oleum at room temperature in order to record the NMR spectrum. This solution deposited a large quantity of fine scarlet-red crystals, which were washed with liquid SO₂. A few red-brown crystals formed from the pale-green SO₂ washings. We report here the X-ray analysis of the red-brown crystals which shows that

they have the composition Se₁₀[SO₃F]₂ and contain the previously reported Se₁₀²⁺ cation (Burns, Chan, Gillespie, Luk, Sawyer & Slim, 1980) as a fluorosulfate salt. The other products obtained in this series of reactions have not yet been identified.

Experimental. Dark red-brown crystals of Se₁₀[SO₃F]₂ occur as blocks and needles. Crystals selected and sealed in Lindemann capillaries in a dry-box equipped with a microscope. Crystal 0.360 × 0.170 × 0.188 mm in the [100], [011] and [01 $\bar{1}$] directions. Precession photographs used to obtain preliminary cell and space-group information. Accurate unit-cell dimensions by least-squares refinement of 2θ , ω and χ for 15 high-angle ($25 < 2\theta < 29^\circ$) reflections on a Syntex P2₁ diffractometer, Mo $K\alpha$ radiation. Data collected using $\theta:2\theta$ scans over a range ($K\alpha_1 - 0.9^\circ$) to ($K\alpha_2 + 0.9^\circ$). Scan rates varied between 3.0 and 29.3° min⁻¹ depending on intensity of preliminary count. Stationary background counts measured at each end of the scan, each for one quarter of the scan time. Three standard reflections obtained after every 67 reflections showed a gradual decrease in intensity with time. 4176 reflections (including standards) in the quadrants $h,k,\pm l$ with $2\theta < 55^\circ$. Lorentz and polarization corrections were applied to all data after the measured intensities had been rescaled to allow for the crystal decomposition (max. rescale factor 1.15). The density was not deter-