Hexanitrometallates. Part IV. Semiconductivity[1]

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Dark current resistivities and activation energies are reported for compressed pellets of $A_2A'M(NO_2)_6$ for a wide range of metals, A, A' and M. The complexes have resistivities of 10^9 to 10^{12} ohm m at 300 K and activation energies of 0.9 to 1.3 eV, except for compounds containing Co^{II} or Co^{III}. $A_3Co^{III}(NO_2)_6$ have resistivities of 10^{12} ohm m, but give curved Arrhenius plots. $A_2A'Co^{II}(NO_2)_6$ have resistivities about 10^5 ohm m and activation energies about 0.5 eV. The behaviour of mixed crystals containing Co^{II} and Co^{III}, or Co^{II} and La^{III} has been investigated. Up to 50% replacement of Co^{II} by Co^{III} produced no significant change in resistivity or activation energy. A mechanism involving hopping by Co^I and Co^{III} species is postulated to explain the enhanced conductivity of the Co^{II} complexes.

Introduction

There are a very large number of hexanitrite complexes $A_2A'M(NO_2)_6$. Most of these compounds are either isomorphous with $K_2BaCo(NO_2)_6$, which has a face centred cubic structure at room temperature, or show only small distortions from this structure type.[2,3,4,5] The optical electron transfer spectra occurring with various combinations of A, A' and M have been discussed in a recent paper.[1] The ease and variety of these optical electron transfer processes suggested the present study of these compounds as semi-conductors.

Experimental

Compounds were prepared as described previously.[6,7] Mixed crystals of $Cs_2(Ba,Na)(Co^{II}Co^{III})(NO_2)_6$ were prepared by adding $Na_3Co(NO_2)_6$ during the preparation of $Cs_2BaCo^{II}(NO_2)_6$ under nitrogen. Mixed crystals of $Cs_2(Ba,Na)(Co^{II},Co^{III})(NO_2)_6$ were prepared by adding cobalt(II)nitrate during the preparation of $Cs_2NaLa(NO_2)_6$ under nitrogen. X-ray powder dia-

grams of the mixed compounds indicated that only a single, face-centred cubic, phase was present in each case (Table I).

Conventional 2-electrode conductivity measurements were made using a Carwyn Instruments voltage supply and either an E.I.L. 33B "Vibron" electrometer or a Keithley 600B electrometer. Checks showed that consistent results were obtained from the two electrometers and the two electrode materials used.

Seebeck coefficients were measured using an apparatus similar to that described by Atkinson and Day,[8] using the Keithley electrometer. Experimental scatter limited the accuracy of the Seebeck coefficients to about 10%.

Measurements of semi-conductivities and Seebeck coefficients were made on pellets pressed at 2400 pound inch^{-2}, using plated gold electrodes or painted silver paste electrodes. Pellets were heated to 410 K before use to remove superficial water. After this initial heating any pellet which did not give reproducible ohmic characteristics at fields below 1.5×10^5 V m^{-1} was rejected. An atmosphere of dry nitrogen flowing at 100 cm^3 min^{-1} was maintained throughout.

TABLE I. Unit Cell Parameters, a, for Mixed $A_2(A',A'')$ $(M,M')(NO_2)_6$ and Related Pure Compounds.

	Mole fraction Co^{II}	a (Å)
$Cs_2(Na,Ba)(Co^{III},Co^{II})(NO_2)_6$	0.5	10.87 ± 0.01
$Cs_2(Na,Ba)(La,Co^{II})(NO_2)_6$	0.15	11.18 ± 0.01
$Cs_2Ba(Ni^{II},Co^{II})(NO_2)_6$	0.3	10.93 ± 0.01
$Cs_2Ba(Cu^{II},Co^{II})(NO_2)_6$	0.5	10.93 ± 0.01
$Cs_2Ba(Ni^{II},Cu^{II})(NO_2)_6$	0.1	10.89 ± 0.01
$Cs_2NaLa(NO_2)_6$ [a]		11.24 ± 0.01
$Cs_3Co(NO_2)_6$ [b]		11.15 ± 0.01
$K_2BaCo(NO_2)_6$ [c]		10.66 ± 0.01

[a] A. Ferrari, L. Cavalca and M. Nardelli, *Gazzetta.*, *81*, 1082 (1951). [b] A. Ferrari and C. Colla, *Atti. Accad. Lincei Rend.*, *17*, 390 (1933). [c] J. A. Bertrand and D. A. Carpenter, *Inorg. Chem.*, *5*, 514 (1966).

Results

The compounds can only be otained as microscopic cubes or octahedra (5–100 μm on edge), so that measurements were, perforce, made on compressed pellets. Pellets of all the samples obeyed Ohm's Law at low applied fields, those containing Co^{II} were non-Ohmic[9] for applied fields in excess of 1.5×10^5 V m⁻¹. Except for the Co^{III} compounds discussed below all the compounds obeyed equations of the form $\log\sigma_T = \log\sigma_O + 2.303 \ E_A/RT$ (Figure 1).

Table II shows that compounds containing cobalt(II) were distinguished from those containing nickel(II), copper(II), iron(II), cadmium(II), lanthanum(III), cerium(III) or bismuth(III) by very much lower resistivity and lower activation energy (Co^{II}, $R_{300} \sim 10^5$ ohm m, $E_A \sim 0.45$ eV; other metal ions $R_{300} \sim 10^9$–10^{12} ohm m, $E_A \sim 1.0$ eV). The values obtained for $A_2A'Co^{II}(NO_2)_6$ were almost independent of A for the potassium, rubidium and caesium salts. In each of the Co^{II} compounds replacement of barium by lead(II) on the A′ site enhanced the conductivity by an order of magnitude and reduced the activation energy slightly.

Both $K_3Co(NO_2)_6$ and $Cs_3Co(NO_2)_6$ showed ohmic behaviour at room temperature but the variation of $\log\sigma$ with 1/T followed a shallow curve (Figure 1).

Since isomorphous substitution is possible over wide composition ranges in $A_2A'M(NO_2)_6$, the conductivity of mixed samples containing Co^{II} has been examined.

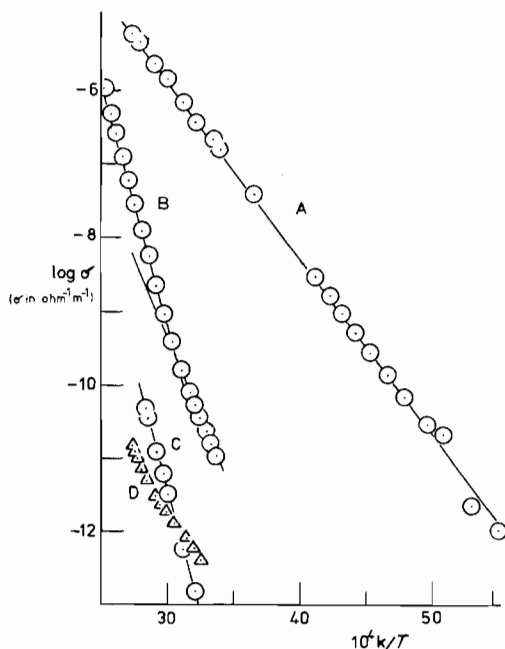Figure 1. Arrhenius plots for semiconductivity of hexanitrometallates. A, $Cs_2BaCo^{II}(NO_2)_6$. B, $Cs_2(Ba,Na)(Co^{II},La)(NO_2)_6$; 20 mole per cent cobalt(II). C, $Cs_2NaCe(NO_2)_6$. D, $Cs_3Co^{III}(NO_2)_6$.

TABLE II. Semiconductivity of $A_2A'M(NO_2)_6$ Complexes.

$A_2A'M$	$R_{300\ K}$/ohm m	E_A/eV	Temp. RangeK
K_2BaCo^{II}	3.0×10^6	0.47	294–415
K_2PbCo^{II}	1.5×10^5	0.41	294–415
Rb_2BaCo^{II}	4.0×10^7	0.55	294–417
Rb_2PbCo^{II}	7.4×10^5	0.42	285–417
Cs_2BaCo^{II}	3.2×10^6	0.48	175–360
Cs_2PbCo^{II}	5.8×10^5	0.47	204–370
Cs_2CsCo^{III}	1.2×10^{12}	(0.6)[a]	303–370
K_2KCo^{III}	$8.0 \times 10^{10\ b}$	(0.7)[a]	300–400
Tl_2BaCu	4.2×10^9	0.91	294–417
K_2PbCu	1.4×10^{10}	1.09	286–384
K_2PbNi	$1.0 \times 10^{12\ b}$	0.96	280–370
K_2CdNi	2.7×10^9	0.82	277–370
Cs_2NaLa	$8.5 \times 10^{10\ b}$	1.25	312–370
Cs_2NaCe^{III}	2.5×10^{12}	1.31	294–357
Cs_2NaBi^{III}	$4.0 \times 10^{10\ b}$	1.10	312–370
Cs_2CdCd	$2.5 \times 10^{10\ b}$	0.94	270–370
K_2PbFe	$1.0 \times 10^{10\ b}$	1.08	294–370

[a] E_A at 300 K from curved plot of $\log\sigma$ against $1/T$. [b] Silver paste electrodes, all other data refer to gold electrodes.

TABLE III. Semiconductivity of Mixed $A_2(A',A'')(M,M')(NO_2)_6$ Complexes.

	Mole fraction Co^{II}	$R_{300\ K}$/ ohm m	E_A/eV
$Cs_2(Ba,Na)(Co^{II},Co^{III})$	1.0	3.2×10^6	0.47
	0.95	9.0×10^5	0.45
	0.80	1.0×10^7	0.49
	0.50	1.4×10^6	0.43
	0.30	1.1×10^8	0.56
$Cs_2(Ba,Na)(Co^{II},La^{III})$	0.50	6.7×10^8	0.52
	0.20	5.2×10^{10}	0.92
			1.31[a]
	0.10	4.0×10^{11}	0.85
			1.10[a]
	0.08	3.3×10^{12}	0.95
			1.24[a]
	0.05	1.8×10^{14}	1.02
			1.48[a]
$Cs_2Ba(Ni^{II},Co^{II})$	0.30	2.5×10^{-10}	0.50[b]
$Cs_2Ba(Cu^{II},Co^{II})$	0.50	5.0×10^{-10}	0.71[b]
$Cs_2Ba(Ni^{II},Cu^{II})$	0.10 (Cu)	5.0×10^{-11}	1.10[b]
$Cs_2Ba(Ni^{II},Cu^{II})$	0.80 (Cu)	5.0×10^{-11}	0.78[b]

[a] Above 340 K. [b] Silver paste electrodes. All other data refer to evaporated gold electrodes.

Table III shows that the introduction of up to 50 mole per cent cobalt(III) into $Cs_2BaCo^{II}(NO_2)_6$ made no significant difference to the resistivity or the activation energy. At 70% cobalt(III) both resistivity and activation energy were intermediate between those of $Cs_2BaCo^{II}(NO_2)_6$ and $Cs_3Co^{III}(NO_2)_6$. Addition of Co^{II}

TABLE IV. Seebeck Coefficients of $A_2A'Co(NO_2)_6$ at 300 K.

$A_2A'M$	S/mVK^{-1}
Cs_2BaCo^{II}	+0.11
Cs_2PbCo^{II}	+0.024
K_2PbCo^{II}	+0.10
Rb_2BaCo^{II}	+0.14

to $Cs_2NaLa(NO_2)_6$ reduced both the resistivity and the activation energy of the host. A slight but reproducible discontinuity appeared in the variation of conductivity with temperature of these samples (Table III). Addition of nickel(II) or copper(II) to $Cs_2BaCo(NO_2)_6$ gave samples of high resistivity. The $(Ni + Co^{II})$ sample had an activation energy within the range for the pure Co^{II} compounds, but the $(Cu + Co^{II})$ sample gave an activation energy of 0.71 eV, lying between the values for pure Co^{II} and pure Cu^{II} compounds.

Seebeck coefficient measurements were carried out on four Co^{II} compounds (Table IV). The values lie between +0.02 and +0.14 mV deg^{-1}. The temperature variation of the Seebeck coefficient of $Rb_2BaCo(NO_2)_6$ was too small to measure on the apparatus available, the upper limit can not exceed 0.001 mV deg^{-2} over the temperature range 290–328 K. Capacitance problems thwarted attempts to measure Seebeck coefficients for the high resistance samples.

Discussion

Explanations are required for several features of these results.

(1) When M in $A_2A'M(NO_2)_6$ is Ni^{II}, Cd^{II}, Fe^{II}, Cu^{II}, La^{III}, Ce^{III} or Bi^{III} the complexes are uniformly poor conductors.

(2) When M is Co^{II} the conductivity is several orders of magnitude greater. This is accompanied by a lower activation energy and a small positive Seebeck coefficient.

(3) Dilution of the Co^{II} compounds makes little difference to conductivity or activation energy as long as the Co^{II} concentration exceeds about 50 mole per cent. Further dilution alters the activation energy and produces a concentration dependence of conductivity.

(4) Replacement of barium ions in $A_2BaCo^{II}(NO_2)_6$ by lead(II) ions enhances the conductivity by an order of magnitude and reduced the activation energy slightly. Similar effects are not observed on the introduction of lead(II) or thallium(I) into the nickel or copper complexes.

It is not possible to offer a completely satisfactory explanation on all these points. In part this is because single crystals were not available large enough for conductivity or Hall effect measurements. Activation ener-

gies from pellet measurements are usually reliable,[8,10] but the resistivity values should not be treated as absolute, particularly for the high resistance samples. Other workers[8] have reported satisfactory Seebeck measurements under similar conditions on comparable materials.

The powders $A_2A'M(NO_2)_6$ compress without fusion to give pellets of low mechanical strength for which the practicable thickness range, 0.6–0.8 mm, is too small to determine the variation of conductivity with path length. The consistency of the data in Table I suggests that at least the gross difference between the cobalt(II) samples and the rest is not due to surface effects.

Cobalt Compounds

The enhancement of the conductivity of $Cs_2A'Co(NO_2)_6$ when A' is lead(II) rather than barium is reminiscent of the increase in conductivity[10] between $K_3Fe(CN)_6$ $(R_{293} = 10^9$ ohm m$)$ and $Tl_3Fe(CN)_6$ $(R_{293} = 4 \times 10^7$ ohm m$)$. In that case Tl^{II} charge carriers arise from the reaction

$$Tl^I + Fe(CN)_6^{3-} \rightarrow Tl^{II} + Fe(CN)_6^{4-} \qquad (1)$$
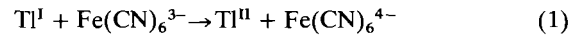
and these Tl^{II} species migrate by electron hopping through the lattice. The activation energy of $Tl_3Fe(CN)_6$ is half that of $K_3Fe(CN)_6$.

The present case is not identical. $A_2BaCo(NO_2)_6$ is itself a good conductor and $A_2PbCo(NO_2)_6$ is only an order of magnitude better with a minimal change in activation energy. It seems more appropriate to involve the Pb^{II} in a carrier migration step than in carrier formation. Reaction of an electron deficient charge carrier with Pb^{II} would give a non-carrier and a Pb^{III} species which could continue the conduction chain by accepting an electron from another potential carrier. Suitable carriers for this reaction must be available in $A_2A'Co^{II}(NO_2)_6$. These carriers must also migrate by a mechanism independent of the A' ion.
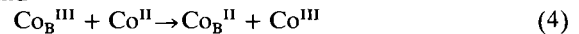
Low spin cobalt(II) $(t_{2g}^6 e_g^1)$ can pass by one electron steps without spin reversal into low spin cobalt(III) $(t_{2g}^6 e_g^0)$ or cobalt(I) $(t_{2g}^6 e_g^2)$. A thermal reaction

$$Co_A^{II} + Co_B^{II} \rightarrow Co_A^I + Co_B^{III} \qquad (2)$$

would create two potential charge carriers, representing "electron" and "hole" respectively. These carriers could migrate by

$$Co_A^I + Co^{II} \rightarrow Co_A^{II} + Co^I \qquad (3)$$

and

$$Co_B^{III} + Co^{II} \rightarrow Co_B^{II} + Co^{III} \qquad (4)$$
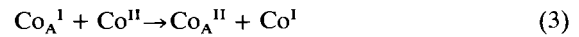
These electron transfer processes must be "outersphere" since each cobalt ion is surrounded by six nitrite ligands and no sharing of ligands occurs between adjacent $Co(NO_2)_6^{4-}$ units.

Day and co-workers have shown that a "hopping" model gives a satisfactory description of conductivity in

metal complexes where localised wave functions are appropriate.[8,11]

The Seebeck coefficient can be expressed[8] by

$$S = -(k/e)(t_e - t_h)E_f/kT$$

where t is the transport number for "electron" or "hole" conduction. A value for S as small as $+0.1$ mV deg^{-1} indicates that $t_e \cong t_h$. In a good conductor this shows that charge carriers of both signs must contribute substantially to the overall conduction process. The migration steps 3 and 4 are independent of each other, so that a zero value for S would be fortuitous.

The chemical addition of $Co(NO_2)_6{}^{3-}$ to $A_2A'Co(NO_2)_6$ does not enhance the conductivity of the sample. The Co^{III} charge carrier is an excited species not physically identical with a stable $Co(NO_2)_6{}^{3-}$. Local vibrational excitation occurs as the average bond length adjusts from the initial (Co^{II}–N) distance towards a typical (Co^{III}–N) bond length. The added $Co(NO_2)_6{}^{3-}$ do not have the vibrational perturbation needed for them to act as charge carriers.

Each charge carrier can continue to move as long as there is a continous path of Co^{II} ions. As in other systems,[8] the activation energy is independent of the concentration of Co^{II} except as low concentrations where the pathway is broken and the activation energy approaches that of the major constituent (Table III).

Since $t_e \cong t_h$, equation 1 suggests that the conductivity in dilute samples will be proportional to the square of the concentration of cobalt(II). Figure 2 shows that
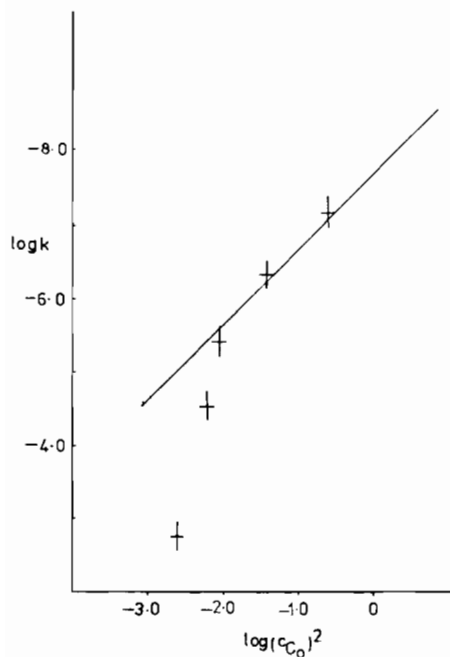

Figure 2. Concentration dependence of conductivity in Cs$_2$(Na,Ba)(La,Co^{II})(NO$_2$)$_6$. The line drawn has unit slope.

this is so, within the experimental error, for Co^{II} doped into $Cs_2NaLa(NO_2)_6$ except at very low concentrations of Co^{II} when space-charge limitation occurs[8] and the conductivity falls very rapidly.

The model represented by reactions 1–3 is consistent with all the evidence available in the conductivity of the cobalt(II) samples. It is also consistent with the optical electron transfer spectra of these compounds, in which the following transitions have been identified:[1]

|	σ/cm^{-1}	Assignment
Cs$_2$BaCo(NO$_2$)$_6$	24,000	$Co^{II} \leftarrow (NO_2{}^-)_6$
Cs$_2$PbCo(NO$_2$)$_6$	19,000	$Co^{II} \leftarrow Pb^{II}$
Tl$_2$BaCo(NO$_2$)$_6$	19,000	$Co^{II} \leftarrow Tl^{I}$

Each of these transitions produces a Co^I excited state. There are several unassigned transitions between 20,000 and 30,000 cm^{-1} in $A_2A'Co(NO_2)_6$ at least one of which is likely to be $[(NO_2{}^-)_6 \leftarrow Co^{II}]$, giving a Co^{III} excited state.[12] The transition in $Cs_2PbCo(NO_2)_6$ at 19,000 cm^{-1} is comparable with a thermal reaction of carrier formation

$$Co^{II} + Pb^{II} \rightarrow Co^I + Pb^{III}$$
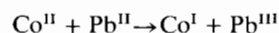
which could act as an additional carrier source. However since the activation energy for conduction decreases only marginally from $Cs_2BaCo(NO_2)_6$ to $Cs_2PbCo(NO_2)_6$ these carriers are probably not important. Carrier migration steps will not correspond to optical transitions in these systems, but the ease of creation of Pb^{III} as an optical excited state is consistent with the use of Pb^{III} as a charge carrier. Although reactions 1–3 are written for metal ions only, the nitrite ligands are not innocent bystanders since they can accept or donate electrons to the metal ions.

Non-cobalt Compounds

Since the compounds of nickel(II), copper(II), iron(II), cadmium(II), bismuth(III), lanthanum(III) and cerium(III) have similar E_A and R_{300} values there is no reason to postulate more than one mechanism for conduction common to all. The introduction of lead(II) or thallium(I) does not enhance the conductivity or alter the activation energy of copper(II) or nickel(II) samples, although optical electron transfer bands assigned to ($M^{II} \leftarrow Pb^{II}$) are seen in both cases.[1] Reaction 5 cannot be a significant source of charge carriers in these compounds.

$$M_A{}^{II} + M_B{}^{II} \rightarrow M_A{}^I + M_B{}^{III} \tag{5}$$
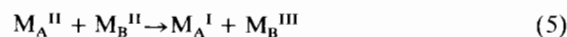
The residual, small conductivity could be described by ionic migration through the lattice[9] as in $KZnCo(CN)_6$ or by a narrow band model.[8] This residual conductivity is clearly insensitive to the composition of the complex $A_2A'M(NO_2)$. The conduction paths do not depend on localised oxidation states of the metal ions.

Acknowledgments

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