

Determination of Pd(II) and Pt(II) Metal Cyano Complexes Using Capillary Electrophoresis

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Received July 5, 1994

Mixtures of cyano complexes of palladium(II) and platinum(II) were separated by capillary electrophoresis using a fused silica capillary as a separation column and 30 mM phosphate buffer (pH 7) containing 15 wt. % acetonitrile as a running buffer. By virtue of the high ionic mobilities of the negatively charged cyano complexes of Pd(II) and Pt(II), they were separated using a cathodic injection and anodic detection scheme. The metal complexes eluted through the capillary were detected by direct UV absorption at 214 nm. A linear relationship between peak area and concentration was obtained for both ions and the detection limit was lower than 10^{-14} mole. The proposed method was applied to real sample, e.g., anode slime obtained from an electrolytic copper refinery, as a method for the simultaneous determination of palladium and platinum.

Introduction

Capillary electrophoresis (CE) has become a powerful and important technique for the separation and determination of charged species.

The majority of CE applications have aimed at separating biological macromolecules, such as amino acids^{1,2} and polynucleotides^{3,4}. Recently, however, several interesting approaches to the separation of inorganic ions^{5,6} and other low molecular weight ionic species^{7,8} have been developed with the help of the CE methodology.

The approach to the determination of metal ions by CE is the formation of metal complexes. In this metal-complex methods, the ligands chosen are usually a widely reactive species capable of forming very stable complexes which have suitably high molar extinction coefficients in order to facilitate direct UV detection. Typical ligands are β -diketones⁹, 4-(2-pyridylazo)resorcinol¹⁰ and 8-quinolinol¹¹. However, there are few reports^{9,12} on the application of CE to transition metal complexes, particularly for platinum group metals (PGMs).

The present work deals with the determination of palladium(II) and platinum(II) after conversion to their cyano complexes without any chelating agent, followed by CE separation. About 30 metal ions are capable of forming cyano complexes including some precious metals. However, the formation of the cyano complexes of PGMs in aqueous solution was difficult except Pd. In the case of Pt, the stable cyano complex was prepared by reducing Pt(IV) to Pt(II) by using hydroxylamine hydrochloride prior to the complexation with cyanide. The method developed in this work is shown to be suitable for the simultaneous determination of palladium and platinum in pg range.

Experimental

Instrumentation. CE was performed with a DIONEX CES-I system (Dionex, USA) and laboratory-made CE (Korea Research Institute of Standards and Science; KRISS) system. Dionex CES-I system was equipped with high voltage power supply of 0-30 kV with reversible polarity and fitted with

a fused silica capillary of 75 μm *i.d.* and 54 cm effective length. KRISS-built CE system was equipped high voltage power supply (Model PS/EH 40R 2.5CTZR, Glassman High Voltage Whitehouse Station, USA) and Model CV⁴ variable wavelength UV detector (ISCO, Inc., Lincoln, NE) and fitted with a fused silica capillary of 50 μm *i.d.* and 56 cm effective length (Polymicro Technology, U. S. A.). Detection was carried out by on-column measurement of direct UV absorption at 214 nm.

Reagents. Stock solution of chloro complexes of Pd(II), Pd(IV), Pt(II) and Pt(IV) were prepared using potassium salts of tetrachloropalladate(II), hexachloropalladate(IV), tetrachloroplatinate(II) and hexachloroplatinate(VI) (Aldrich, USA). Analytical grade potassium tetracyanopalladate(II) trihydrate (Aldrich), potassium tetracyanoplatinate(II) trihydrate (Aldrich), potassium cyanide (Tokyo Showa, Japan) and hydroxylamine hydrochloride (J. T. Baker, USA) were used without further purification.

Preparation of test solution and electrophoretic buffer. Test solutions of tetracyanopalladate(II) and tetracyanoplatinate(II) were prepared as follows: 1 ml of 0.1 M hydroxylamine hydrochloride as reducing agent was added to 1 ml of slightly acidic solution containing the corresponding metal chloro complex (1×10^{-3} M) and then 1 ml of 0.3 M KCN was added. The solution was diluted to final volume of 10 ml with distilled water.

The electrophoretic buffer was disodium hydrogen phosphate and sodium dihydrogen phosphate mixture containing acetonitrile. The pH of the electrophoretic buffer was adjusted by changing the ratio of NaH_2PO_4 and Na_2HPO_4 . Peaks of metal complexes eluted with the borate buffer were very small because of high background absorption of borate at 214 nm. Accordingly, phosphate buffer was used in subsequent studies. All solutions (electrolytes and samples) were prepared using 18 M Ω water generated by a Milli-Q laboratory water purification system (Millipore, USA). All electrolytes were prepared daily, filtered with a membrane filter of 0.22 μm pore size and degassed prior to use.

Preparation of the sample solution for copper refinery anode slime. For the analysis of anode slime ob-

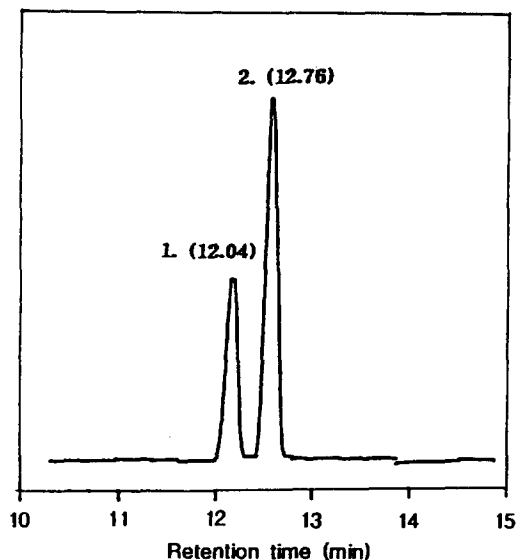


Figure 1. Typical electropherogram of cyano complexes of Pd(II) and Pt(II). Phosphate buffer (30 mM, pH 7) containing 15 wt. % acetonitrile; 75 μm i.d. \times 67 cm capillary; applied voltage, 20 kV; detection wavelength, 214 nm; metal concentration, 1×10^{-4} M., 1. $[\text{Pd}(\text{CN})_4]^{2-}$, 2. $[\text{Pt}(\text{CN})_4]^{2-}$.

tained from an electrolytic copper refinery, the sample was dried at 110 $^\circ\text{C}$ for 2 hrs.. 0.187 g of sample was gently heated with 10 ml aqua regia until it was completely decomposed. After cooling, 10 ml of concentrated hydrochloric acid was added and the mixture was evaporated almost to dryness, and finally dissolved in 10 ml of 1 N hydrochloric acid, followed by filtering (Whatman No. 40) into a 100 ml volumetric flask and diluted to the mark with water. To 1.0-2.0 ml aliquot of the sample solution, 1 ml of 0.1 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ and 2 ml of 0.25 M KCN were added. The resulting solution was heated on a hot plate for 15 min at 80 $^\circ\text{C}$. After cooling to room temperature, the solution was diluted to 10.0 ml with water.

Results and Discussion

Experimental methodology

In a typical CE system with a fused-silica capillary, the direction of the electroosmotic flow is usually from the anode to the cathode and the sample is injected at the anode. The electroosmotic flow-rate is often so strong that all the analytes, even those with negative charge, will move toward the cathode. In this work, however, the electrophoretic mobilities of the negatively charged metal cyanides are so large that they will not be carried from the anode to the cathode, making their detection impossible if they are injected at anode. Consequently, we employed the use of a "reverse movement"^{12,13} mode as follows: we injected the sample at the cathode and placed the detector near the anode. Under these conditions, the species of interest, the negatively charged metal complexes, migrated toward the anode against the electroosmotic flow.

A typical electropherogram of tetracyanopalladate(II) and tetracyanoplatinate(II) ions are shown in Figure 1. The concentration of each metal complex was 1×10^{-4} M. As can

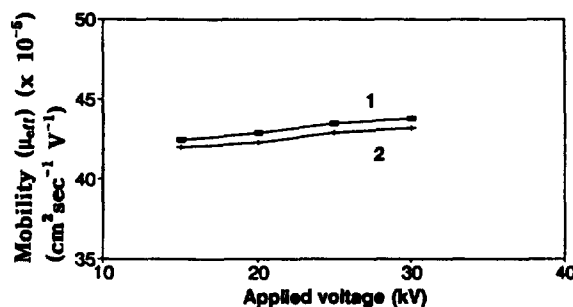


Figure 2. Effect of the applied voltage on the mobilities (μ_{eff}). Phosphate buffer (30 mM, pH 7); other conditions were same as in Figure 1., 1. $[\text{Pd}(\text{CN})_4]^{2-}$, 2. $[\text{Pt}(\text{CN})_4]^{2-}$.

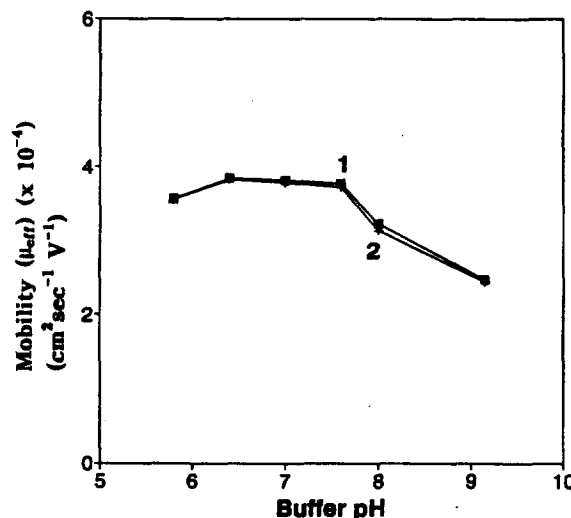


Figure 3. pH effect of phosphate buffer on the mobilities (μ_{eff}). Phosphate buffer (30 mM); other conditions were same as in Figure 1., 1. $[\text{Pd}(\text{CN})_4]^{2-}$, 2. $[\text{Pt}(\text{CN})_4]^{2-}$.

be seen from Figure 1, peaks were well separated within approximately 13 min for total elution.

Applied voltage

The effect of applied voltage on the mobilities, μ_{eff} of the Pd(II) and Pt(II) cyano complexes is illustrated in Figure 2.

As shown in Figure 2, the values, μ_{eff} of $[\text{Pd}(\text{CN})_4]^{2-}$ and $[\text{Pt}(\text{CN})_4]^{2-}$ increased by approximately 0.25%/kV with increasing applied voltage (V). This is probably because the temperature of the carrier in the capillary was elevated by the Joule heating: as a rule, the value μ_{eff} (absolute value) increase by 2% for each 1 $^\circ\text{C}$ increase in temperature¹⁴. High applied voltage appears to be preferable for short analysis time. However, applied voltage of 20 kV was chosen as it gave low signal-to-noise ratio (S/N) as compared to higher voltage.

pH of electrophoretic buffer

The pH dependence of the mobilities, μ_{eff} of the cyano complexes of Pd(II) and Pt(II) in 30 mM phosphate buffer was shown in Figure 3. The mobilities of the complexes were fairly constant below pH 7.5, but they decreased above pH

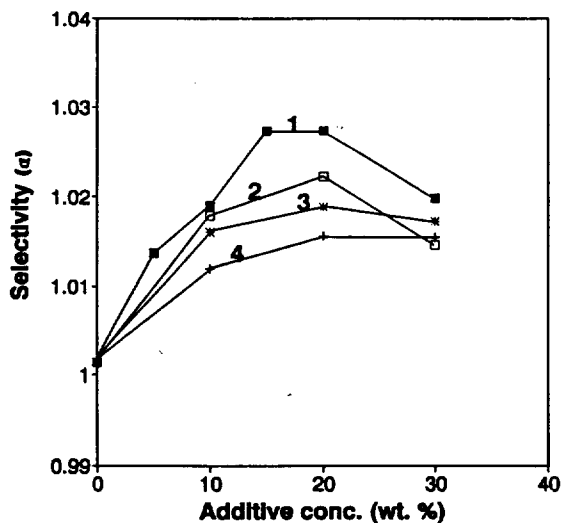


Figure 4. Effect of the additives on the selectivity of cyano complexes of Pd(II) and Pt(II). Phosphate buffer (30 mM, pH 7)+additives: 1. acetonitrile, 2. methanol, 3. ethanol, 4. isopropanol. Other conditions were same as in Figure 1.

7.5. This result is also ascribable to the effect of the electroosmotic mobility being influenced by change in the ionic strength.

Effect of additives in buffer

Initial studies with electrophoretic buffers containing no additives showed that palladium(II) and platinum(II) complexes have poor resolution. To improve separation of Pd(II) peak from that of Pt(II), organic modifiers, such as acetonitrile, methanol, ethanol and isopropanol were added to the running buffers.

It has been reported¹⁵ that organic modifiers, such as acetonitrile and methanol help reduce interaction of the analyte with the charged silanol groups of the capillary wall. This factor can cumulatively help to minimize tailing and increase the resolution of the analyte peaks.

The effects of these additives on the selectivity of Pd(II) and Pt(II) cyano complexes are given in Figure 4. The results show that the best selectivity for the separation of Pt(II) and Pd(II) was obtained in the buffer containing 15-20 wt. % acetonitrile. At the same condition, when methanol was used in place of acetonitrile, the band widths of the eluted peaks of Pd(II) and Pt(II) cyano complexes became narrower. However, the selectivity became inferior as compared to acetonitrile as shown in Figure 4. The phosphate buffer containing 15 wt. % acetonitrile was, therefore, used for subsequent work.

The chloro complexes of Pd and Pt

Since Pd and Pt chloro-complexes are easily obtained by dissolution of real samples, we attempted to determine the Pd and Pt as their chloro-complexes.

The electropherogram in Figure 5(a), which showed no peak, was obtained for chloro complexes of Pd(II), Pd(IV) and Pt(II). As shown in Figure 5(b), one peak from the chloro complex of Pt(IV) appeared in the electropherogram that was obtained from the freshly prepared solution. However, after

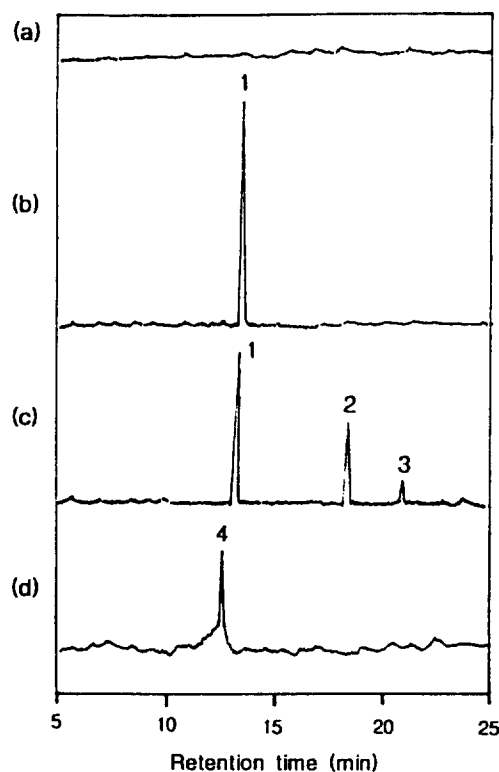


Figure 5. Electropherogram of chloro complexes of Pd and Pt. (a) $[\text{PdCl}_4]^{2-}$, $[\text{PdCl}_6]^{2-}$ and $[\text{PtCl}_4]^{2-}$, (b) fresh solution of $[\text{PtCl}_6]^{2-}$, (c) aged solution of $[\text{PtCl}_6]^{2-}$ (d) the solution (c) + 100 mM KCN.; other conditions were same as in Figure 1. Peaks: 1. $[\text{PtCl}_6]^{2-}$, 2 and 3. $[\text{PtCl}_5(\text{OH})]^{2-}$ or $[\text{PtCl}_5(\text{H}_2\text{O})]^{-}$, 4. $[\text{Pt}(\text{CN})_4]^{2-}$.

standing over 24 hours, the same solution gave two or more peaks as shown in Figure 5(c). This phenomenon seems to indicate that the ionic species of chloro complex of Pt(IV) changed with time. Therefore, this can probably be explained as follows: these chloro species may undergo stepwise aquation to varying extents in neutral solution¹⁶. Therefore, the peak 2 and 3 in Figure 5(c) may be assigned to be anionic species of general formula $[\text{PtCl}_5(\text{H}_2\text{O})]^{-}$ or $[\text{PtCl}_5(\text{OH})]^{2-}$, which may exist at about pH 7. Thus, the Pd and Pt chloro-complexes are not able to be used for simultaneous determination of Pd and Pt.

As shown in Figure 5(d), when 100 mM cyanide were presented in this aged solution, the peaks of Pt(IV) chloro complexes disappeared, and a single peak of $[\text{Pt}(\text{CN})_4]^{2-}$ was obtained.

The formation of Pd and Pt cyano complexes

In order to prepare the cyano complexes of Pd(II) and Pt(II), 1 ml of 300 mM KCN were added to the solution containing Pd(IV) and Pt(IV) chloro complexes, and the cyanide concentration in the final solution was 30 mM. The electropherogram was shown in Figure 6(b): three peaks were obtained. In order to determine which of the peaks should be assigned to the Pd(II) and Pt(II) complexes, the sample solution was spiked with the standard solutions of tetracyanopalladate(II) and tetracyanoplatinate(II). This eluted peaks indicated that the chloro complexes of Pd(IV) and Pt(IV) in 30 mM KCN were transformed to the anionic com-

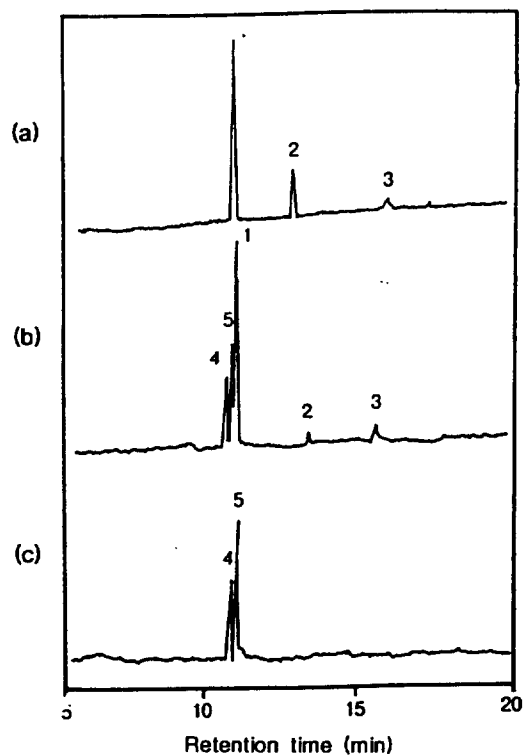


Figure 6. Electropherogram of chloro complexes of Pd(IV) and Pt(IV) in KCN system. (a) aged solution of $[\text{PdCl}_6]^{2-}$ and $[\text{PtCl}_6]^{2-}$, (b) the solution (a)+30 mM KCN, (c) the solution (a)+10 mM $\text{NH}_2\text{OH}\cdot\text{HCl}$ +30 mM KCN; other conditions are same as in Figure 1, 1. $[\text{PtCl}_6]^{2-}$, 2 and 3. $[\text{PtCl}_5(\text{OH})]^{2-}$ or $[\text{PtCl}_5(\text{H}_2\text{O})]^{-}$, 4. $[\text{Pd}(\text{CN})_4]^{2-}$ 5. $[\text{Pt}(\text{CN})_4]^{2-}$.

plexes of formula $[\text{Pd}(\text{CN})_4]^{2-}$, $[\text{Pt}(\text{CN})_4]^{2-}$ and $[\text{PtCl}_6]^{2-}$. By the reduction of Pt(IV) using hydroxylamine hydrochloride as reducing agent, the chlorocomplexes of Pd(IV) and Pt(IV) in 30 mM KCN solution were completely transformed to the anionic complexes of formula $[\text{Pd}(\text{CN})_4]^{2-}$ and $[\text{Pt}(\text{CN})_4]^{2-}$, respectively as shown in Figure 6(c). The identity of these complexes was also confirmed by UV absorption spectra.

Determination of Pd and Pt in anode slime obtained from an electrolytic copper refinery

Reproducibility and linear range. Several consecutive runs were performed to confirm both the reproducibility of the migration time and the linearity of the peak areas with concentration. The migration times were found as follows: 722.4 ± 2.4 sec for $[\text{Pd}(\text{CN})_4]^{2-}$ and 765.6 ± 2.7 sec for $[\text{Pt}(\text{CN})_4]^{2-}$.

A linear relationship was obtained between peak area and concentration over the concentration range from 1×10^{-4} M to 1×10^{-7} M for both Pd and Pt.

The reproducibility in the migration times as well as the correlation coefficient ($r > 0.999$) of the calibration curve indicate that CE can be used for both qualitative and quantitative analysis of cyano complexes of Pd and Pt.

Quantitation and detection limits. Quantitation of palladium and platinum in copper refinery anode slime were done by both calibration method and standard addition meth-

Table 1. Analytical data of anode slime obtained from an electrolytic copper refinery

Method	Pd (mg/g)	Pt (mg/g)
Calibration	38.6	3.68
	38.1	3.50
	37.2	3.48
	37.0	3.79
	37.5	3.92
	37.2	3.69
	38.6	3.68
mean	37.7 (± 0.4)	3.68 (± 0.12)
Std. Add.	36.6	3.76
ICP-AES	37.4 (± 0.1)	3.62 (± 0.12)

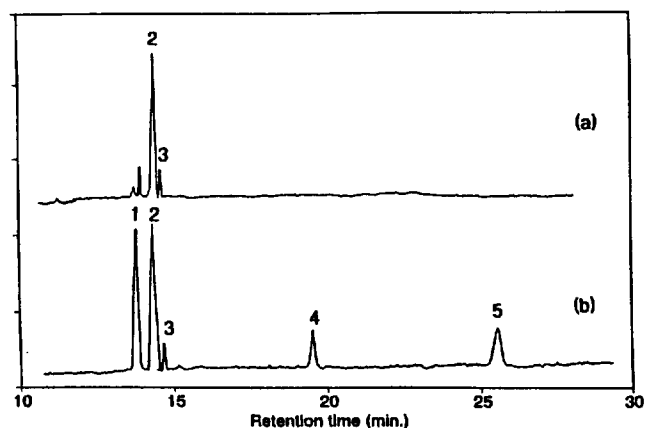


Figure 7. Electropherogram of anode slime obtained from an electrolytic copper refinery. (a) Anode slime. (b) the solution (a) + 3×10^{-4} M Ni(II) + 3×10^{-4} M Cu(II) + 3×10^{-4} M Co(II). Conditions were same as in Figure 1, 1. Ni(II), 2. Pd(II), 3. Pt(II), 4. Cu(II), 5. Co(II).

od. The results with CE in Table 1 are compared with those obtained for the same samples by inductively coupled plasma atomic emission spectrometry (ICP-AES). These values are in good agreement with the analytical results obtained from ICP-AES.

Detection limits (a signal-to-noise ratio of 3) correspond to absolute amount of 2.5×10^{-14} mole for Pd and 6.6×10^{-15} mole for Pt (2.7 pg and 1.3 pg, respectively) in a 40 nL injection. These absolute detection limits are about 10^3 times lower than that obtained in ion-pair HPLC (7.5×10^{-12} mole and 4.6×10^{-12} mole in a 100 μL injection).¹⁷

Effects of matrix. The electropherogram in Figure 7(a) contains peaks of palladium and platinum of a sample taken from copper refinery anode slime. The electropherogram (b) represents that of the anode slime sample to which nickel, copper and cobalt were added. This figure indicated that palladium(II) and platinum(II) can be determined simultaneously in the presence of ca. 300 times of these transition metals without matrix interferences.

Conclusion

An analytical method using capillary electrophoresis was

developed for the simultaneous determination of Pd(II) and Pt(II) as their cyano complexes. The method provides good sensitivity of ca. 2 pg with extremely small quantity of sample (ca. 40 μ l) as well as simple analytical procedure.

The present CE methodology was applied to a real sample, e.g., anode slime obtained from an electrolytic copper refinery. The analytical data obtained for Pd and Pt were in accord with those obtained independently by the inductively coupled plasma atomic emission spectrometry.

Acknowledgment. We gratefully acknowledge that the present study was supported by the grant BSRI-93-339, from the Ministry of Education and by Division of Chemistry, Korea Research Institute of Standards and Science*.

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The LS→HS Transition of Cobalt(III) in an Oxygen Lattice with the K₂NiF₄-Type Structure: Correlations with the Chemical Bonding Environment of the (CoO₆) Octahedron Along the c-axis

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Received June 7, 1994

In oxides characterized by the K₂NiF₄-type structure, the low-spin→high-spin transition of trivalent cobalt ion was studied in function of the nature of competing bonds in the perovskite-plane and along the c-axis. Using Slichter and Drickamer's model the calculated values of parameters characterizing such a transition are correlated with the covalency of competing bonds along the c-axis of the K₂NiF₄-structure and the local structural distortion of the (CoO₆) octahedron.

Introduction

During last twenty years, a lot of studies involving the spin-state transition in cobalt(III) oxides have been carried out. The first oxygen lattice selected was the three-dimensional perovskite structure ACoO₃ (A=rare earth)^{1,2}, or A₂M'CoO₆ (A=Sr, Ba; M'=Sb)^{3,4}. The cobalt(III) oxides with the layered structure derived from the K₂NiF₄-type have been also recently investigated⁵.

The change of electronic configurations of transition metal ions versus temperature is an interesting phenomenon due to the modifications of the induced magnetic properties. Co-

balt(III) seems to be a good candidate, the low-spin state being characterized by a ¹A_{1g} diamagnetic ground term and the high-spin state by a paramagnetic ⁵T_{2g} one (in O_h symmetry).

The oxides with general formula (A, A')₂(M, M')O₄ appeared to be a good model for evaluating the influence of the different chemical bonding factors on the low-spin(LS)→high-spin(HS) transition, the (MO₆) octahedron being surrounded by two types of competing bonds:

- (M'-O) in the perovskite-plane
- [(A, A')-O] along the c-axis (Figure 1).

Such competing bonds can anisotropically modify the cova-