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Tetranitratometallates of Manganese(II), Cobalt(II), Nickel(II), and Copper(II)

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A new series of compounds of the general formula $M(NO_3)_4^{-2}$ are reported in which M is Mn(II), Co(II),[2] Ni(II), and Cu(II). The compounds are synthesized from a non-aqueous solvent and isolated as methyltriphenylarsonium salts. Spectral and magnetic data are interpreted to indicate the structures of these complexes. The anions formed with copper and nickel contain bidentate chelate or bridging nitrate groups and the metal ions have an environment that is nearly octahedral. Data on the cobalt complex indicate a tetrahedral structure. The crystal field parameters *Dq* and β are reported for nitrate ion toward nickel(II). The infrared spectra of the anions are similar to those reported for coördinated nitrate ion.

Introduction

There is very little research reported on anionic transition metal ion complexes containing nitrate as the sole ligand. Only a few have been isolated in the solid form. Addison and Hodge have reported ethylammonium tetranitratozincate, an extremely deliquescent compound, prepared by the reaction of zinc metal with ethylammonium nitrate in liquid dinitrogen tetroxide.[3] Although the formulation of some dinitrogen tetroxide addition compounds of metal nitrates, such as $Co(NO_3)_2 \cdot 2N_2O_4$, as $(NO)_2[Co(NO_3)_4]$ is open to doubt,[4] the iron complex,[5] $Fe(NO_3)_3 \cdot N_2O_4$, very probably has the structure $NO[Fe(NO_3)_4]$.[5] An investigation of the infrared spectrum of the well known compound $K_2Ce(NO_3)_6$ indicates that the nitrate group has C_{2v} symmetry.[6] The nitrate is in the first coördination sphere of the metal ion and there is polarization of one of the nitrogen–oxygen bonds by the Ce(IV). Complexes of the type $M(NO_3)_3 \cdot 2(C_6H_5)_4PNO_3$, where M = La, Ce, Pr, and Nd, were prepared by Medoks and Sakharova.[7] Although the structures of these compounds have not been determined, it seems likely that the nitrate ion is coördinated to the metal ion.

Our interest in the use of non-aqueous solvents for the synthesis of compounds that cannot be prepared in water[8,9] has led to the discovery of convenient preparations for a series of compounds of the general formula $M(NO_3)_4^{-2}$. This paper describes the preparation and some physical properties of hexakis-(dimethyl sulfoxide)-cobalt(II) tetranitratocobaltate(II), and methyltriphenylarsonium salts of the anions: tetranitratocobaltate(II), tetranitratomanganate(II), tetranitratonickelate(II), and tetranitratocuprate(II). The large cations, $[Co(DMSO)_6]^{+2}$ (DMSO = dimethyl sulfoxide) and $[(C_6H_5)_3AsCH_3]^+$, stabilize the large nitrato anions in the crystal lattice. The compounds were prepared by a metathetical reaction between silver nitrate, methyltriphenylarsonium iodide (or dimethyl sulfoxide) and the anhydrous metal chloride or bromide in acetonitrile

$$MCl_2 + 2(C_6H_5)_3AsCH_3I + 4AgNO_3 \longrightarrow [(C_6H_5)_3AsCH_3]_2[M(NO_3)_4] + 2AgCl + 2AgI$$

Spectral and magnetic data are presented to indicate that the tetranitratometallates of Cu(II) and Ni(II) are six-coördinate complexes. The spectra of the complexes are similar to spectra characteristic of octahedral complexes. This is common for tetragonal complexes with very slight tetragonal distortion.[10] The anions must contain bridging (or chelate) and terminal nitrate groups

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[1] Abstracted in part from the Ph.D. Thesis of D. K. Straub, University of Illinois, 1961.

[2] Subsequent to submission of this manuscript a communication appeared by F. A. Cotton and T. G. Dunne in *J. Am. Chem. Soc.*, **84**, 2013 (1962), describing the cobalt complex.

[3] C. C. Addison and N. Hodge, *J. Chem. Soc.*, 1138 (1954).

[4] C. C. Addison and B. J. Hathaway, "Addition Compounds of Dinitrogen Tetroxide and Their Application in Preparative Inorganic Chemistry," in "Recent Aspects of the Inorganic Chemistry of Nitrogen," Special Publication No. 10, The Chemical Society, London, 1957.

[5] C. C. Addison and B. J. Hathaway, *J. Chem. Soc.*, 1468 (1960).

[6] J. R. Ferraro, *J. Mol. Spectry.*, **4**, 99 (1960).

[7] G. V. Medoks and N. N. Sakharova, *Dokl. Akad. Nauk SSSR*, **73**, 1201 (1950).

[8] D. W. Meek, D. K. Straub, and R. S. Drago, *J. Am. Chem. Soc.*, **82**, 6013 (1960).

[9] J. T. Donoghue and R. S. Drago, *Inorg. Chem.*, **1**, 866 (1962).

which interact in a similar[10] fashion with the metal ion.

Experimental

Reagents.—All starting materials were reagent grade. Acetonitrile, methylene chloride, chloroform, and carbon tetrachloride were distilled from phosphorus(V) oxide before use. The dimethyl sulfoxide was stored over "Drierite" for several days with occasional shaking, then distilled under reduced pressure and stored in a desiccator. Anhydrous nickel(II), cobalt(II), and manganese(II) chlorides were prepared from the corresponding hydrates by dehydration at 120°. Methyltriphenylarsonium iodide was prepared by refluxing a solution of triphenylarsine in a large excess of methyl iodide for a few hours. The excess methyl iodide was removed by evaporation; the residue was extracted repeatedly with ether to remove unreacted triphenylarsine, and then dried at 120°.

Hexakis-(dimethyl sulfoxide)-cobalt(II) Tetranitratocobaltate(II).—Seventeen g. (0.1 mole) of silver nitrate, dissolved in 20 ml. of acetonitrile, was added to a solution of 6.5 g. (0.05 mole) of anhydrous cobalt(II) chloride in 75 ml. of acetonitrile. The precipitated silver chloride was removed by filtration and 12 g. (0.15 mole) of dimethyl sulfoxide was added to the deep purple-red filtrate. Addition of 300 ml. of ether precipitated a red oil which was kept *in vacuo* overnight. The moist crystalline mass was recrystallized from methylene chloride; the crystals were washed with ether and dried at 56° *in vacuo* for 1 hr. Care was taken throughout to exclude moisture, since the deep purple-red crystals were extremely deliquescent.

Anal. Calcd. for $Co(NO_3)_2 \cdot 3(CH_3)_2SO$: C, 17.27; H, 4.32; N, 6.71. Found: C, 16.67; H, 4.18; N, 6.76.

Methyltriphenylarsonium Tetranitratocobaltate(II).—Powdered silver nitrate (6.8 g., 0.04 mole) was added to a mixture of 1.3 g. (0.01 mole) of anhydrous cobalt(II) chloride and 9.0 g. (0.02 mole) of methyltriphenylarsonium iodide in about 30 ml. of acetonitrile. The mixture was magnetically stirred until the reaction was complete (about 5 min.), then centrifuged to remove the precipitated silver chloride and iodide. The liquid was evaporated to about half its original volume and an excess of ether was added. The oil which separated was stirred and soon became crystalline. The crystals were washed twice by decantation with ether, dried at room temperature *in vacuo*, and redissolved in methylene chloride. The solution again was centrifuged to remove traces of silver salts, and evaporated to dryness. The compound was recrystallized from a methylene chloride–chloroform mixture to give well formed, deep purple crystals. These were dried at room temperature *in vacuo*.

Anal. Calcd. for $(C_{19}H_{18}As)_2[Co(NO_3)_4]$: C, 48.07; H, 3.82; N, 5.90. Found: C, 48.06; H, 3.67; N, 6.08.

Methyltriphenylarsonium Tetranitratomanganate(II).—A mixture of 1.26 g. (0.01 mole) of anhydrous manganese(II) chloride, 6.8 g. (0.04 mole) of silver nitrate, and 9.0 g. (0.02 mole) of methyltriphenylarsonium iodide in about 25 ml. of acetonitrile was stirred until reaction was complete. The precipitated silver halides were removed by centrifugation. The colorless solution was evaporated *in vacuo* until colorless crystals separated. These were removed, dried at room temperature *in vacuo*, and redissolved in acetonitrile. The solution again was centrifuged to remove traces of insoluble silver salts, and evaporated until crystals formed. (Since this compound was less soluble in methylene chloride than the other compounds reported in this paper, it was more conveniently recrystallized from acetonitrile.) These crystals were removed, washed once with acetonitrile, three times with ether, and dried at room temperature *in vacuo*. Again, care was taken throughout to avoid exposure to moisture. The colorless crystals were very deliquescent.

Anal. Calcd. for $(C_{19}H_{18}As)_2[Mn(NO_3)_4]$: C, 48.27; H, 3.84; N, 5.93. Found: C, 47.38; H, 3.98; N, 6.00.

Methyltriphenylarsonium Tetranitratonickelate(II).—A mixture of 1.3 g. (0.01 mole) of anhydrous nickel(II) chloride, 6.8 g. (0.04 mole) of silver nitrate, and 9.0 g. (0.02 mole) of methyltriphenylarsonium iodide in about 25 ml. of acetonitrile was stirred until reaction was complete. After removal of the precipitated silver halides by centrifugation, the green liquid was evaporated to dryness *in vacuo* at room temperature. The crystals so obtained were redissolved in a small amount of methylene chloride (in which the compound is very soluble), and the solution again was centrifuged to remove traces of silver salts. Carbon tetrachloride was added until the solution became slightly turbid. The flask was stoppered and allowed to stand. Large green colored crystals slowly formed. The compound was very deliquescent.

Anal. Calcd. for $(C_{19}H_{18}As)_2[Ni(NO_3)_4]$: C, 48.08; H, 3.82; N, 5.90; Ni, 6.18. Found: C, 48.17; H, 3.81; N, 5.90; Ni, 6.28.

Methyltriphenylarsonium Tetranitratocuprate(II).—A mixture of 1.1 g. (0.005 mole) of anhydrous copper(II) bromide, 3.4 g. (0.02 mole) of silver nitrate, and 4.5 g. (0.01 mole) of methyltriphenylarsonium iodide in about 20 ml. of acetonitrile was stirred until reaction was complete and then centrifuged to remove precipitated silver halides. The solution was evaporated to dryness, the crystals were dissolved in methylene chloride, and the resulting solution was centrifuged to remove traces of silver salts. The blue solution was evaporated to a small volume *in vacuo* at room temperature. The blue crystals which formed were removed, washed with methylene chloride and ether, and dried *in vacuo*. The compound appeared to be non-deliquescent.

Anal. Calcd. for $(C_{19}H_{18}As)_2Mn(NO_3)_4$: C, 47.84; H, 3.81; N, 5.87. Found: C, 47.51; H, 3.74; N, 6.03.

Spectral Measurements.—Electronic spectral data were obtained with a Cary (Model 14M) recording spectrophotometer. Solid reflectance spectra were obtained with a Bausch and Lomb Spectronic 505 recording spectrophotometer with standard reflectance attachment. Blocks of $MgCO_3$ were employed as standards. Infrared spectra of mulls of the solid compounds were made with a Perkin-Elmer Model 21 recording spectrophotometer with sodium chloride optics.

Magnetic Measurements.—Magnetic susceptibilities were determined by the Gouy method, utilizing a Newport Type C electromagnet. The Gouy tubes were calibrated using $Hg[Co(NCS)_4]$ as described by Figgis.[11] The moments reported are room temperature values (30°) cor-

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[10] C. K. Jørgenson, "Energy Levels of Complexes and Gaseous Ions," Gjellerups, Copenhagen, 1957.

[11] B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958).

TABLE I

ELECTRONIC SPECTRAL DATA FOR $[(C_6H_5)_3AsCH_3]_2[M(NO_3)_4]$ AND OTHER COMPLEXES

Complex	Medium	λ_{max}, mμ	ν_{max}, cm.$^{-1}$	Reference
$[(C_6H_5)_3AsCH_3]_2[Co(NO_3)_4]$	Solid, reflectance	540	18,500	[a]
	Nitromethane (0.0045 *M*)	538 (107)[b]	18,500	[a]
$[Co(H_2O)_6]^{+2}$	H_2O	513 (4·8)	19,500	15
		454 (sh)	22,000	
$[(C_6H_5)_3AsCH_3]_2[Cu(NO_3)_4]$	Solid, reflectance	400	25,000	[a]
		700	14,300	
	Nitromethane (0.0009 *M*)	400	25,000	[a]
		785 (6.05)	12,750	
$Cu(H_2O)_6^{+2}$	H_2O	800 (13)	12,500	15
$[(C_6H_5)_3AsCH_3]_2[Ni(NO_3)_4]$	Solid, reflectance	420	23,800	[a]
		700	14,300	
	Nitromethane	415 (11.0)	24,100	[a]
		698 (4.05)	14,300	
		760 (sh)	13,150	
		1,250 (1.80)	8,000	
$[Ni(DMSO)_6]^{+2}$	DMSO	416	24,038 (10.15)[b]	8
		700	14,286 (2.54)	
		770	12,970 (3.68)	
		1,295	7,728 (3.48)	
$[(C_6H_5)_3AsCH_3]_2[Mn(NO_3)_4]$	Solid, reflectance	410	24,400	[a]
		450 (sh)	22,200	
		530 (sh)	18,900	

[a] Designates this work. [b] Numbers in parentheses designate value of molar extinction coefficient at band maximum.

rected for diamagnetic contributions. The values for Pascal's constants were obtained from the literature[12] and applied to the experimental moments as diamagnetic corrections.

Results

The electronic spectra of nitromethane solutions of the methyltriphenylarsonium tetranitratometallates of Cu(II), Co(II), Ni(II), and Mn(II) are summarized in Table I and presented graphically in Fig. 1. Solid reflectance spectra in the visible (400–700 mμ) range are included in Table I and presented in Fig. 2.

Magnetic moments for the solid compounds at room temperature (30°), corrected for diamagnetic contributions, are presented in Table II. The diamagnetic contribution of Mn(II) was assumed to be the same as those of Cu(II), Co(II), and Ni(II) at 12.8×10^{-6}.

Assignments of infrared frequencies were made with the aid of reported literature values. The assignments should be considered tentative, due to difficulties arising from cation absorbance in the pertinent regions. The data are presented in Table III.

TABLE II

MAGNETIC MOMENTS FOR $[(C_6H_5)_3AsCH_3]_2[M(NO_3)_4]$ (30°)

M	$\chi_M \times 10^6$	Diamag. cor. $\times 10^6$	$\chi_M' \times 10^6$	μ_{eff} B.M.
Cu(II)	1255	283	1538	1.93 ± 0.06
Co(II)	8655	283	8938	4.67 ± 0.04
Ni(II)	3792	283	4075	3.15 ± 0.04
Mn(II)	13312	283	13595	5.76 ± 0.04

Discussion

Although the stoichiometric ratio of NO_3^- to metal ion is 4 to 1 in these compounds, the electronic spectra of $Ni(NO_3)_4^{-2}$ shown in Fig. 1 and 2 are interpreted in terms of six-coördinate nickel(II). The similarity in the spectrum of this ion and $Ni(DMSO)_6^{+2}$ is obvious from the data in Table I. The ϵ_{max} and λ values are in good agreement with those for typical octahedral Ni(II) complexes. The ratio of the frequencies of the transitions $[{}^3A_{2g} \rightarrow {}^3T_{2g}\ (F)]$ and $[{}^3A_{2g} \rightarrow {}^3T_{2g}]$ for $Ni(NO_3)_4^{-2}$ also supports a near octahedral structure. Analysis of the spectral data of tetranitratonickelate(II) for the parameter *Dq* yielded the surprising result that NO_3^- occupies a position in the spectrochemical series slightly lower than water and greater than that of Cl^- and DMSO.[13] The

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[12] B. N. Figgis and J. Lewis, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, ed., Interscience, New York, N. Y., 1960, p. 403.

[13] D. W. Meek, R. S. Drago, and T. S. Piper, *Inorg. Chem.*, **1**, 285 (1962).

TABLE III

INFRARED SPECTRAL DATA FOR TETRANITRATOMETALLATES

Compound	ν_6	ν_2	ν_1	ν_4	$(\nu_4 - \nu_1)$
$[Co(DMSO)_6][Co(NO_3)_4]$	811	1022	Obscured by DMSO	Obscured by DMSO	
$[(C_6H_5)_3CH_3As]_2[Co(NO_3)_4]$	807	1022	1285	1462	177
$[(C_6H_5)_3CH_3As]_2[Mn(NO_3)_4]$	813	1028	1283	1463	180
$[(C_6H_5)_3CH_3As]_2[Ni(NO_3)_4]$	805	1019	1270	1465	195
$[(C_6H_5)_3CH_3As]_2[Cu(NO_3)_4]$	805	1013	1290	1465	175

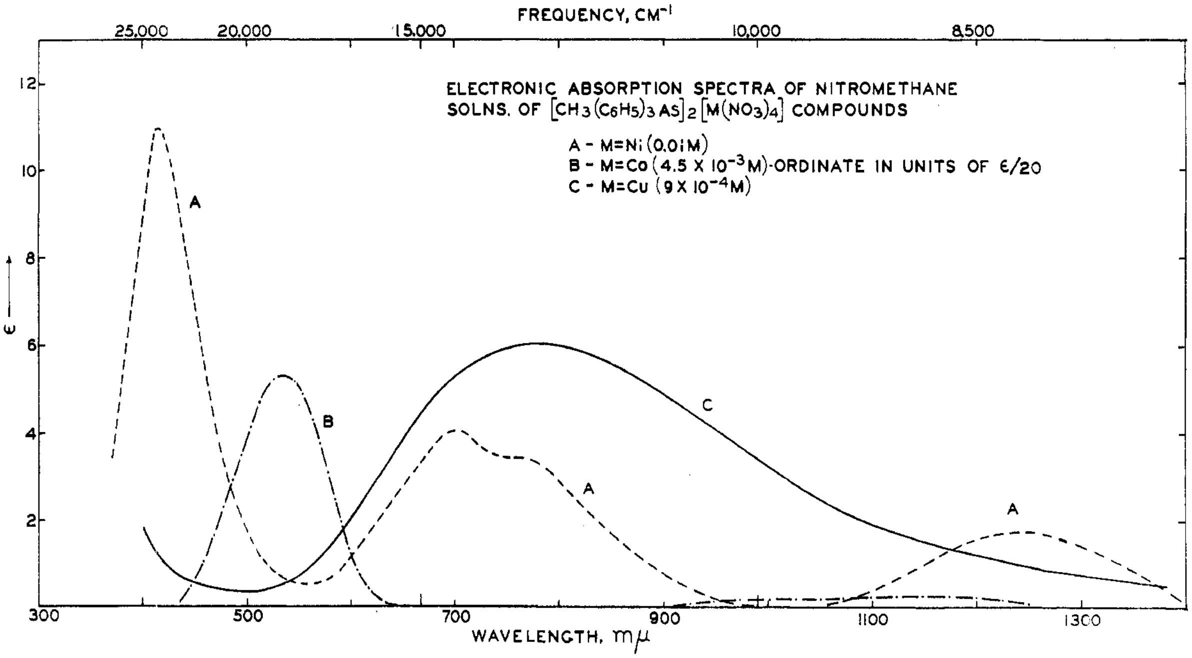

Figure 1.

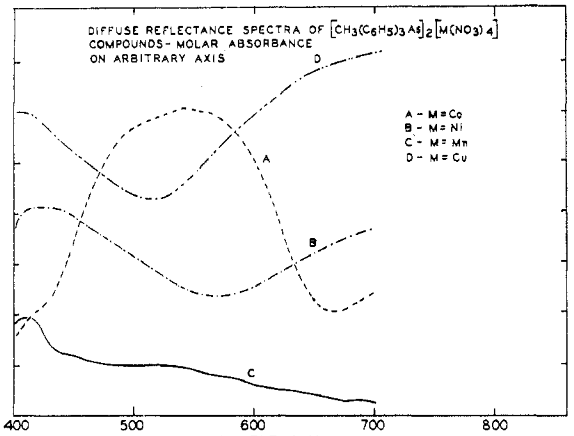

Figure 2.

following Dq values are reported toward nickel(II): H_2O (860) > NO_3^- (801) > DMSO (773) > Cl^- (720). The β values[14] indicate that there is more covalency in the metal ion–nitrate bond than in the metal ion–water bond. Chloride ion is appreciably more covalent. The following β values are reported: Cl^- (26%) > NO_3^- (15%) > H_2O (12%).

To obtain an octahedral field, the NO_3^- ion must serve as a bridging or chelate group. The spectra indicate that any tetragonal distortion is not large. The fields imposed by terminal and bridging nitrate groups are then not very different, since any great differences would manifest themselves in the spectra.[10]

The magnetic moment of the Ni(II) complex is in the range expected for octahedral Ni(II).[15]

The visible spectrum of tetranitratocobaltate consists of a single broad absorption of intermediate intensity. The value of ϵ_{max} (107) suggests tetrahedral rather than octahedral coördination, though the intensity is somewhat lower than "typically" found for tetrahedral Co(II). The magnetic moment (4.67 B.M.) also is in accord with tetrahedral Co(II).

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[14] β is defined as the percentage reduction in the P–F term in the complex compared to the gaseous ion.

[15] B. N. Figgis, *Nature*, **182**, 1568 (1958).

The major evidence for the structural assignment for $Cu(NO_3)_4^{-2}$ is the spectral data. Magnetic data are not expected to differentiate between octahedral and tetrahedral arrangements. The low ϵ value for the maximum and the band position for the Cu(II) complex are in accord with those found for $Cu(H_2O)_6^{+2}$.[16] The observed intensity is very much lower than those observed for square planar Cu(II).

The infrared spectra indicate that the nitrate ion is coördinated in these ions. Free nitrate ion has D_{3h} symmetry. Upon coördination this symmetry is lowered to C_{2v}, causing a splitting of the ν_3 frequency (NO_2 asymmetric stretch) of the nitrate ion into a higher frequency, ν_4 (NO_2 asymmetric stretch), and a lower frequency, ν_1 (NO_2 symmetric stretch). The difference in wave numbers between ν_4 and ν_1 is reported to increase with an increase in the covalent contribution to the bonding. Application of this criterion to our data is not appropriate because the spectra were run on solids and the complexes contain bridging nitrate groups. A ν_2 frequency (NO stretch) which is inactive for ionic nitrate and a ν_6 frequency (nonplanar rock) also appear. A number of papers have appeared recently on the infrared spectra of free and coördinated nitrate.[17-19] With the data now available, an unambiguous assignment of the symmetry of the nitrate group in most compounds can be made.

In Table III infrared spectral data are reported for the ions $[Co(NO_3)_4]^{-2}$, $[Mn(NO_3)_4]^{-2}$, $[Ni(NO_3)_4]^{-2}$, and $[Cu(NO_3)_4]^{-2}$. No bands occur which are assignable to free nitrate ion. The differences, $\nu_4 - \nu_1$, indicate that the nitrate is coördinated to the metal. It is interesting to compare these differences with the values of $\nu_4 - \nu_1$ found for $Hg(NO_3)_2$ (119 cm.$^{-1}$), $Zn(NO_3)_2$ (200–250 cm.$^{-1}$), $Mn(NO_3)_2$ (259 cm.$^{-1}$), $Cu(NO_3)_2$ (250–300 cm.$^{-1}$), $K_2[Ce(NO_3)_6]$ (244 cm.$^{-1}$), and CH_3ONO_2 (385 cm.$^{-1}$).[7,18]

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(16) N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959).

(17) B. M. Gatehouse, S. E. Livingstone, and R. S. Nyholm, *Ibid.*, 4222 (1957).

(18) C. C. Addison and B. M. Gatehouse, *ibid.*, 613 (1960).

(19) J. R. Ferraro, *J. Inorg. Nucl. Chem.*, **10**, 319 (1959).

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Multidentate Ligand Kinetics. II. Zinc(II) and Ethylenediaminetetraacetatonickelate(II) with Copper(II) Catalysis

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The Zn^{+2} substitution reaction with nickel-EDTA[1] is $^1/_{6500}$ times as fast as the corresponding Cu^{+2} reaction at 25.0°. However, the same type of kinetic expression is found for Zn^{+2} and Cu^{+2} as contrasted to radionickel exchange and their relative rate constants permit the path of this type of substitution reaction to be characterized. A dinuclear reaction intermediate is proposed with an iminodiacetate segment of EDTA coördinated to the attacking metal ion. The catalysis of the Zn^{+2} reaction by traces of Cu^{+2} is studied.

Introduction

In a previous paper[2] the kinetics of the copper(II) reaction with the nickel-EDTA complex were shown to be quite different from the corresponding radionickel reaction. In this work zinc ion like nickel ion is found to be sluggish in its attack on nickel-EDTA, but unlike nickel ion the zinc reaction is pH independent between pH 3 and 5. Thus, the kinetic dependence of the zinc ion is similar to that of copper ion. This permits their relative electrophilic ability to be related to the reaction intermediate (previously proposed) to determine which segments of EDTA initially bound to nickel are coördinated to the attacking metal ion.

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(1) Ethylenediaminetetraacetic acid.

(2) T. J. Bydalek and D. W. Margerum, *J. Am. Chem. Soc.*, **83**, 4326 (1961).