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The Effect of Acetate Ion on the Reaction between Copper(II) and the Ethylenediaminetetraacetatonickelate(II) Ion

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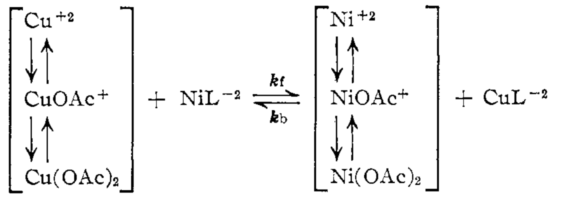
The kinetics of the substitution reaction between the mono- and diacetate complexes of copper(II) and the ethylenediaminetetraacetatonickelate(II) ion have been studied at several pH values at an ionic strength of 1.25 maintained with sodium perchlorate. The temperature dependence of both forward and reverse rates has been determined. In the forward reaction, the formation of acetate complexes of copper(II) causes a decrease in reaction rate, whereas in the reverse reaction, an increase in reaction rate is observed. These differences are compared to similar exchange systems and discussed in terms of proposed dinuclear reaction intermediates and the rates of loss of water from the hydrated and complexed ions.

Introduction

The kinetics of the reactions of hydrated copper(II) and zinc(II) with the ethylenediaminetetraacetatonickelate(II) ion have been investigated[1-3] and explained in terms of proposed dinuclear ethylenediaminetetraacetate, EDTA or L, reaction intermediates. These systems were studied in the absence of any buffer to avoid the effects of other complexing agents. The kinetics of similar systems[4-6] were investigated in the presence of strong acetate buffer. The rate of reaction of the hydrated metal ion was not independently measured, and the data were evaluated on the assumption that acetate complexes did not react or that the ratio of the rate constants of the acetate complexes to the rate constant of the hydrated metal ion was a constant for all reaction paths. In the present study, the effect of the acetate ion on the rate of reaction between copper(II) and Ni-EDTA is investigated and compared to similar metal exchange systems.

The system studied is



$$\begin{bmatrix} Cu^{+2} \\ \downarrow\uparrow \\ CuOAc^{+} \\ \downarrow\uparrow \\ Cu(OAc)_2 \end{bmatrix} + NiL^{-2} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \begin{bmatrix} Ni^{+2} \\ \downarrow\uparrow \\ NiOAc^{+} \\ \downarrow\uparrow \\ Ni(OAc)_2 \end{bmatrix} + CuL^{-2} \quad (1)$$

where the acetate complexes are in rapid equilibrium compared to the rate of exchange of the metal ions. The rate of formation of Cu-EDTA can be expressed as

$$\frac{d[CuL]}{dt} = k_f[Cu_T][NiL^{-2}] \quad (2)$$

where $[Cu_T]$ refers to the sum of the concentrations of hydrated copper(II) and the mono- and diacetate complexes of copper(II) at any time.

Experimental

The experimental procedures were similar to those previously reported.[1-3] A constant ionic strength of 1.25 was maintained with sodium perchlorate in order to make comparisons with earlier kinetic studies. Solutions of Na_2NiL and Na_2CuL were prepared by adding excess metal perchlorate to EDTA and precipitating out the excess as the metal hydroxide before adjusting the solutions to pH 5.5. Perchlorate salts were used throughout. Concentrated solutions of sodium acetate and acetic acid were standardized by pH titration with standard hydrochloric acid and sodium hydroxide solutions, respectively. The reaction was followed at the 735 mμ absorption band of Cu-EDTA. The absorbances of all other species are appreciable and were corrected for. The concentration of Cu-EDTA produced during the course of the reaction was calculated from the expression

$$[CuL] = \frac{A - A_i}{b(\epsilon_{CuL} + \epsilon_{Ni_T} - \epsilon_{NiL} - \epsilon_{Cu_T})} \quad (3)$$

The values of A and A_i refer to the observed absorbance and the initial absorbance of the reactants, respectively, corrected for any background absorbance. The cell length, b, was 10 cm. The ϵ terms refer to the individual molar absorptivities of the various species. The terms ϵ_{Ni_T} and ϵ_{Cu_T} refer to the apparent molar absorptivity of the mixture of nickel and copper acetate complexes, respectively, at each acetate concentration. The change in the value of ϵ_{Ni_T} with change in acetate concentration was negligible at 735 mμ under the conditions used. The value of ϵ_{Cu_T} used at each acetate concentration was the weighted average of the individual molar absorptivities of the copper acetate complexes. The values of the individual molar absorptivities of the copper acetate complexes were determined independently from equilibrium mixtures at selected acetate concentrations using the values of the instability constants, K_{CuOAc} and $K_{Cu(OAc)_2}$, previously reported[7] for 1.00 M $NaClO_4$ and 20°. These values are 2.2×10^{-2} and 1.0×10^{-1}, respectively. The corresponding values for the nickel complexes[8] are 2.1×10^{-1} and 2.6×10^{-1}, respectively. The molar absorptivities of Cu-EDTA and Ni-EDTA, ϵ_{CuL} and ϵ_{NiL}, respectively, were measured in the presence of acetic acid–sodium acetate buffer. The concentration of buffer has no effect on these values. In the pH range studied, protonation of Cu-EDTA and Ni-EDTA was not sufficient to change the values of ϵ_{CuL} and ϵ_{NiL} significantly. The values of the molar absorptivities at 735 mμ in units of M^{-1} cm.$^{-1}$ are: NiL^{-2}, 2.5; CuL^{-2}, 102; Ni^{+2}, $NiOAc^{+}$, $Ni(OAc)_2$, 2.1; Cu^{+2}, 9.3; $Cu(OAc)^{+}$, 24.0; and $Cu(OAc)_2$, 34.0. The value of $[OAc^{-}]$ was taken as the amount added since the decrease due to copper acetate formation is always small compared to the total added. As the acetate ion concentration was varied, the acetic

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

[2] D. W. Margerum and T. J. Bydalek, *Inorg. Chem.*, **1**, 852 (1962).

[3] T. J. Bydalek and D. W. Margerum, *ibid.*, **2**, 678 (1963).

[4] H. Ackermann and G. Schwarzenbach, *Helv. Chim. Acta*, **35**, 485 (1952).

[5] S. Bril, K. Bril, and P. Krumholz, *J. Phys. Chem.*, **59**, 596 (1955).

[6] N. Tanaka and M. Kamada, *Bull. Chem. Soc. Japan*, **35**, 1596 (1962).

[7] N. Tanaka and K. Kato, *Bull. Chem. Soc. Japan*, **32**, 1376 (1959).

[8] N. Tanaka and K. Kato, *ibid.*, **32**, 516 (1959).

TABLE I

SECOND-ORDER RATE CONSTANTS FOR COPPER ACETATE ATTACK ON Ni-EDTA

25.0°, $\mu = 1.25$, $[\mathrm{OAc^-}] = 0.10\ M$

pH	[HOAc], M	$[\mathrm{Cu_T}] \times 10^4$, M	$[\mathrm{NiL^{-2}}] \times 10^3$, M	k_f, M^{-1} sec.$^{-1}$ $\times 10^3$
4.30	0.112	3.86	.917	5.6
4.30	0.112	3.86	1.83	5.6
4.30	0.112	3.86	4.58	5.5
4.30[a]	0.112	3.86	9.17	5.6
4.30[b]	0.112	3.86	9.17	5.6
4.30	0.112	7.72	9.17	5.7
4.30	0.112	11.6	9.17	5.5
5.00	0.022	1.93	9.17	5.6
4.00	0.224	7.72	9.17	5.4
				Av. 5.6

[a] Sodium acetate and acetic acid added to $\mathrm{Cu^{+2}}$, followed by Ni-EDTA addition. [b] Sodium acetate and acetic acid added to Ni-EDTA, followed by $\mathrm{Cu^{+2}}$ addition.

acid concentration was also varied to maintain constant pH except where pH variation was desired. The order of addition had no effect on the reaction rate.

The reaction was followed for at least 50% conversion to products and rate constants were reproducible to ±3%. The acid dissociation path of Ni-EDTA was less than 3% in all runs and was neglected. The reverse reaction was also negligible under the conditions used.

Results

Kinetics of the Forward Reaction.—As in the reaction of hydrated copper(II) with Ni-EDTA, the reactions show first-order dependence in $[\mathrm{Cu_T}]$ and [NiL]. Likewise the rate constant is pH independent. Table I shows the constancy of the second-order rate constant as the [NiL], $[\mathrm{Cu_T}]$, and pH are varied at constant $[\mathrm{OAc^-}]$. In most runs, the [NiL] was in large excess and the rates were plotted as pseudo-first-order in $[\mathrm{Cu_T}]$. The decrease in rate as the $[\mathrm{OAc^-}]$ is increased is clearly shown in Table II.

The rate can also be expressed as

$$\frac{\mathrm{d}[\mathrm{CuL}]}{\mathrm{d}t} = k_{\mathrm{Cu}}[\mathrm{Cu^{+2}}][\mathrm{NiL^{-2}}] + k_{\mathrm{CuOAc}}[\mathrm{CuOAc^+}][\mathrm{NiL^{-2}}] + k_{\mathrm{Cu(OAc)_2}}[\mathrm{Cu(OAc)_2}][\mathrm{NiL^{-2}}] \quad (4)$$

so that from eq. 2 and 4 and the values of the copper(II) acetate instability constants

$$k_f\left(1 + \frac{[\mathrm{OAc^-}]}{K_{\mathrm{CuOAc}}} + \frac{[\mathrm{OAc^-}]^2}{K_{\mathrm{CuOAc}}K_{\mathrm{Cu(OAc)_2}}}\right) = k_{\mathrm{Cu}} + k_{\mathrm{CuOAc}}\frac{[\mathrm{OAc^-}]}{K_{\mathrm{CuOAc}}} + k_{\mathrm{Cu(OAc)_2}}\frac{[\mathrm{OAc^-}]^2}{K_{\mathrm{CuOAc}}K_{\mathrm{Cu(OAc)}}} \quad (5)$$

At acetate concentrations below 0.02 M, terms in $[\mathrm{OAc}]^2$ are negligible to within 8%, and a plot of $k_f(1 + [\mathrm{OAc^-}]/K_{\mathrm{CuOAc}})$ *vs.* $[\mathrm{OAc^-}]$ yields a straight line with intercept of k_{Cu} and a slope of $k_{\mathrm{CuOac}}/K_{\mathrm{CuOAc}}$. The value of the intercept, $1.63 \times 10^{-2}\ M^{-1}$ sec.$^{-1}$, is in excellent agreement with that previously reported.[1] The value of k_{CuOAc} obtained from the slope is $5.8 \times 10^{-3}\ M^{-1}$ sec.$^{-1}$.

At high $[\mathrm{OAc^-}]$, eq. 5 can be rearranged to

$$\frac{k_f(1 + [\mathrm{OAc^-}]/K_{\mathrm{CuOAc}} + [\mathrm{OAc^-}]^2/K_{\mathrm{CuOAc}}K_{\mathrm{Cu(OAc)_2}}) - k_{\mathrm{Cu}}}{[\mathrm{OAc}]/K_{\mathrm{CuOAc}}} = k_{\mathrm{CuOAc}} + (k_{\mathrm{CuOAc}}/K_{\mathrm{Cu(OAc)_2}})[\mathrm{OAc^-}] \quad (6)$$

A plot of the left-hand-side of eq. 6 *vs.* $[\mathrm{OAc^-}]$ is linear and the value of k_{CuOAc}, $5.9 \times 10^{-3}\ M^{-1}$ sec.$^{-1}$, obtained from the intercept is in excellent agreement with that determined from the slope at low $[\mathrm{OAc^-}]$. The value of $k_{\mathrm{Cu(OAc)_2}}$ obtained from the slope is $2.8 \times 10^{-3}\ M^{-1}$ sec.$^{-1}$. Over the actual range of acetate concentrations used, 0.005–0.13 M, the relative extent of reaction by each pathway is as follows: $\mathrm{Cu^{+2}}$, 93 to 22%; $\mathrm{CuOAc^+}$, 7 to 48%; $\mathrm{Cu(OAc)_2}$, 0.2 to 30%. The use of the rate constants given above predicts the observed rate constant to within 5% at all acetate concentrations employed. The formation of acetate complexes therefore results in a decrease in rate by the removal of copper(II), but the acetate complexes still contribute to the over-all rate of reaction.

The temperature dependence of k_{CuOAc} and $k_{\mathrm{Cu(OAc)_2}}$ was studied between 15 and 35° at pH 4.30 and an ionic strength of 1.25 by a similar set of kinetic runs. The values of K_{CuOAc} and $K_{\mathrm{Cu(OAc)_2}}$ at 15 and 35° were evaluated spectrophotometrically assuming that the molar absorptivities of the copper acetate complexes are temperature independent. The values obtained were 2.2×10^{-2} and 9.7×10^{-2}, respectively, at 15° and 2.5×10^{-2} and 1.3×10^{-1}, respectively, at 35°. The kinetic results followed the Arrhenius expression and are given in Table III. The error in the values of E_A is 1.5 kcal.

TABLE II

VARIATION OF THE SECOND-ORDER RATE CONSTANT, k_f, WITH ACETATE CONCENTRATION

25.0°, $\mu = 1.25$, pH 4.30, $[\mathrm{NiL^{-2}}] = 9.17 \times 10^{-3}\ M$

$[\mathrm{OAc^-}] \times 10^2$, M	$[\mathrm{Cu_T}] \times 10^4$, M	k_f, M^{-1} sec.$^{-1}$ $\times 10^2$
0.50	1.93	1.44
1.0	1.93	1.30
1.5	3.86	1.21
1.8	3.86	1.17
2.0	1.93	1.11
4.7[a]	29.0	0.76
5.0	1.93	0.75
7.0	3.86	0.65
9.0	3.86	0.60
10.0	3.86	0.56
12.6[a]	29.0	0.50
13.0	3.86	0.49

[a] $[\mathrm{OAc^-}]$ calculated by successive approximation, $[\mathrm{NiL^{-2}}] = 2.9 \times 10^{-3}\ M$.

Kinetics of the Reverse Reaction.—The reverse reaction was studied at 25° and an ionic strength of 1.25 maintained with sodium perchlorate and found to be first order in [CuL] and $[\mathrm{Ni_T}]$. In the reverse reaction, however, increasing $[\mathrm{OAc^-}]$ produces an increase in rate. The data were treated in an analogous manner to those of the forward reaction using values of k_b determined at various acetate concentrations and the values[8] of K_{NiOAc} and $K_{\mathrm{Ni(OAc)_2}}$. The values of k_{NiOAc} and $k_{\mathrm{Ni(OAc)_2}}$ are identical and have a value of 3.8×10^{-2}

TABLE III

TEMPERATURE DEPENDENCE

	Rate constants, M^{-1} sec.$^{-1}$ $\times 10^2$			Kinetic parameters	
	15°	25°	35°	E_A, kcal./mole	A, M^{-1} sec.$^{-1}$ $\times 10^{-12}$
k_{Cu}	0.63	1.63	4.8	18	0.24
k_{CuOAc}	0.21	0.58	1.93	20	2.6
$k_{Cu(OAc)_2}$	0.08	0.28	0.72	20	1.2
k_{Ni}	0.34	1.05	3.3	20	4.7
k_{NiOAc}	1.55	3.8	9.1	16	0.020
$k_{Ni(OAc)_2}$	1.48	3.8	9.7	17	0.11

M^{-1} sec.$^{-1}$. The value of 1.05×10^{-2} M^{-1} sec.$^{-1}$ observed for k_{Ni} is in excellent agreement with that previously reported.[1] The equilibrium constants at 25° calculated from the ratios of k_{CuOAc}/k_{NiOAc} and $k_{Cu(OAc)_2}/k_{Ni(OAc)_2}$, 1.5×10^{-1} and 7.4×10^{-2}, respectively, are in good agreement with the values calculated from the individual equilibrium constants of reactants and products of the equilibria

$$NiL^{-2} + CuOAc^{+} \rightleftharpoons CuL^{-2} + NiOAc^{+}$$

$$NiL^{-2} + Cu(OAc)_2 \rightleftharpoons CuL^{-2} + Ni(OAc)_2$$

The values obtained from equilibrium constant calculations are 1.6×10^{-1} and 6.4×10^{-2}, respectively.

The temperature dependence of k_{NiOAc} and $k_{Ni(OAc)_2}$ was also investigated between 15 and 35°. These results are shown in Table III along with the dependence of the forward rate constants. The values of K_{NiOAc} and $K_{Ni(OAc)_2}$ were not re-evaluated at 15 and 35° due to the very small temperature dependence previously reported.[8]

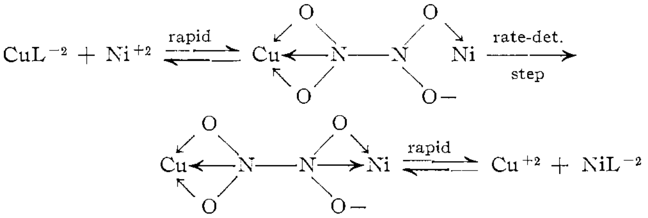
Discussion

The electrophilic substitution reaction between copper(II) and the ethylenediaminetetraacetatonickelate(II) ion has been postulated to proceed through a dinuclear reaction intermediate possessing an iminodiacetate segment of the EDTA molecule bonded to copper and a glycinate segment bonded to nickel.[1-3] This proposed dinuclear species corresponds to an intermediate formed prior to the transition state by partially unwrapping the EDTA from nickel and coordinating it to the attacking metal ion. Furthermore, the most reasonable interpretation of the data indicates that the breaking of the nickel–nitrogen bond is the rate-determining step. Since the observed rate is proportional to the concentration of the intermediate, any complexing agent, such as acetate ion, that can complex with copper will necessarily decrease the rate by the above reaction path by decreasing the concentration of the copper reactant and therefore the reaction intermediate. In addition it is possible that such complexed copper species can enter into the rate as is observed in the $CuOAc^{+}$ and $Cu(OAc)_2$ attack on Ni-EDTA, and similar reaction intermediates can be proposed for these paths. The bonding of the EDTA will be the same but in addition the copper ion will have bonded to it one or two acetate ions. These reaction paths will be of less importance on the basis of both statistical considerations and the lowered stability of the reaction intermediates due to electrostatic considerations. Thus the observed ratios k_{Cu}/k_{CuOAc} and $k_{CuOAc}/k_{Cu(OAc)_2}$ are 2.9 and 2.1, respectively.

Statistical effects can be calculated on the basis of assumed structures by a consideration of the total number of ways in which the intermediate can form. Calculations involving structures assumed on the basis of the preferred stereochemistry of the EDTA molecule[9] and the lowest repulsion between the acetate ions and the acetate groups of the EDTA molecule give a ratio of 2 for both k_{Cu}/k_{CuOAc} and $k_{CuOAc}/k_{Cu(OAc)_2}$.

In addition to the statistical effects, a slower rate might be predicted as a result of repulsive forces between the acetate ions and the acetate groups of the EDTA molecule. Furthermore, it seems that the acetate ions in the coordination sphere could alter the stability of the iminodiacetate segment by changes in the bonding to copper(II). Unfortunately, the magnitude of these interactions cannot be quantitatively calculated. In fact it appears that such effects may be small and that the statistical effects alone account for the observed ratios of rate constants.

The reverse reaction is of greater interest. Here the addition of an acetate ion to nickel(II) causes an increase in reaction rate even though similar factors as present in the forward rate would predict a slower rate of reaction. Assuming that the nickel–nitrogen bond breaking is the rate-determining step in the reaction of copper(II) and Ni-EDTA, the principle of microscopic reversibility dictates that the rate-determining step in the reaction of nickel(II) with Cu-EDTA involves the formation of the nickel–nitrogen bond. Prior to this bond formation the acetate group of EDTA is assumed to be associated with or bonded to the nickel ion. The reaction can be represented as



The observed rate constant,[1] $k_{Ni} = 1.03 \times 10^{-2}$ M^{-1} sec.$^{-1}$, will then be composed of terms involving the stability of the intermediate and the rate constant for nickel–nitrogen bond formation. Furthermore, this rate of bond formation may depend on the rate of water loss from nickel(II). In fact this appears to be the case. Using the values of the stability constants for segments of the EDTA molecule given in ref. 3, the value of the stability constant of the intermediate can be estimated to be 1×10^{-6}. Combining this with the value of k_{Ni}, a value of 1×10^{4} sec.$^{-1}$ can be calculated for the rate constant for nickel–nitrogen bond formation. This value is in agreement with the value of the rate constant for water loss from nickel, 3.2×10^{4} sec.$^{-1}$, determined by Connick and Stover.[10] Hammes

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[9] G. S. Smith and J. L. Hoard, *J. Am. Chem. Soc.*, **81**, 556, (1956). Analogous to Ni-EDTA, it is assumed that the iminodiacetate segment does not lie in one plane.

[10] R. E. Connick and E. S. Stover, *J. Phys. Chem.*, **65**, 2075 (1961).

and Steinfeld[11] in their work on the formation of the glycinate complexes of nickel(II) calculate a rate of water loss from the monoglycinatonickelate(II) complex 13 times greater than that of the aquo nickel ion and attribute the increase to a loosening of the water molecules in the primary hydration sphere due to the reduced net positive charge on the nickel ion. Similarly they found that the diglycinato complex loses water 3.3 times faster than the mono complex. The acetate ion could function in much the same way as the glycinate ion and thus increase the rate of reaction between nickel and Cu-EDTA. Thus $NiOAc^+$ should react 13 times faster than Ni^{+2} with CuL^{-2}. This factor is necessarily decreased by similar statistical and electrostatic effects as described for the forward rate. As before, quantitative calculations cannot be made but if the ratio of k_{Cu}/k_{CuOAc}, 2.9, is taken as a measure of these effects, the predicted ratio of k_{NiOAc}/k_{Ni} is 13/2.9, or 4.5. This is in good agreement with the observed value of 3.6. An analogous calculation for the ratio $k_{Ni(OAc)_2}/k_{NiOAc}$ gives a value of 3.3/2.1, or 1.6, which is in agreement with the observed value of 1.0.

Recently, however, Margerum and Eigen[12] have investigated the rate of replacement of a water molecule by an ammonia molecule in a number of nickel chelate complexes, including Ni-EDTA, and could not correlate these rates with the charge on the complexes. They suggest that the amine nitrogen groups influence the rate of water loss and that chelate rings may also have an effect. On this basis the effect of acetate appears anomalous.

Margerum and Zabin[13] have observed that, when the attacking metal ion is less labile than the metal ion originally bound to EDTA, hydroxide ion greatly accelerates the rate of exchange. They attributed this to an increased rate of water loss from the monohydroxo metal ion. The behavior of the acetate ion in this study parallels this behavior of hydroxide ion, increasing the rate of the less labile nickel ion. The magnitude of its effect is not as great, however.

The opposite effect of the acetate ion, *i.e.*, decreasing the rate of the more labile metal ion, may be indicative that the rate-determining step involves the breaking of original metal–EDTA bonds as in the reactions between copper(II) and the ethylenediaminetetraacetatozincate-(II),[14] -cadmate(II),[4,6] -plumbate(II),[15] and -cobaltate-(II)[16] ions. By analogy to the copper reaction with Ni-EDTA, it can be reasoned that the rate-determining step in these reactions involves the breaking of Zn–, Cd–, Pb–, and Co–EDTA bonds rather than Cu bond formation. Any further designation in rate-determining step in these systems is not possible since sufficient data are not available.

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[11] G. G. Hammes and J. I. Steinfeld, *J. Am. Chem. Soc.*, **84**, 4639 (1962).

[12] D. W. Margerum, personal communication, Aug. 4, 1964.

[13] D. W. Margerum and B. A. Zabin, Abstracts of Papers, 144th National Meeting of the American Chemical Society, Los Angeles, Calif., 1963, p. 6K.

[14] K. Kato, *Bull. Chem. Soc. Japan*, **33**, 600 (1960).

[15] N. Tanaka and K. Kato, *ibid.*, **32**, 1376 (1959).

[16] N. Tanaka, H. Osawa, and M. Kamada, *ibid.*, **36**, 530 (1963).

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Rhenium-Containing Complex Metal Oxides of the Formula Type $A^{II}{}_4Re^{VII}{}_2M^{II}O_{12}$

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The complex oxides of rhenium provide two new examples of layer structures based on the close packing of AO_3 layers. The composition of these oxides is $A_4Re_2MO_{12}$. The Re and the M cations occupy octahedral sites. A 12-layer stacking sequence is adopted for large A and relatively small M cations. For A = Ba, these include M = Mg, Ca, Co, Zn, Cd, and In; for A = Sr, M = Mg, Co, Ni, and Zn. When M is large, particularly relative to A, a 24-layer structure is assumed, which, however, is related to a simpler structure with an 8-layer stacking scheme. Compounds with this structure are $Ba_5Re_2O_{12}$, $Sr_5Re_2O_{12}$, $Sr_4Re_2CaO_{12}$, and $Ca_5Re_2O_{12}$. In both cases face sharing of filled octahedra is avoided by a systematic arrangement of empty octahedra.

Introduction

For complex metal oxides containing large cations in the ratio of one large cation to three oxygens, the structures are often conveniently described on the basis of close-packed AO_3 layers, where A is the large cation. Close-packed stacking of these layers leads to the formation of one octahedron of oxygens for each AO_3 unit. These octahedral sites may be occupied by metal ions or, in some cases, left vacant. A number of known examples and some new possibilities are discussed in a paper by Katz and Ward.[1] Reference was made in this paper to a series of compounds of general formula $A^{II}{}_4Re^{VII}{}_2M^{II}O_{12}$, for which early evidence indicated a 12-layer stacking sequence. In the present paper

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[1] L. Katz and R. Ward, *Inorg. Chem.*, **3**, 205 (1964).