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Kinetics of Metal Exchange in Copper(II) Chelates: Evidence for Dinuclear Intermediate Formation from Steric Effects

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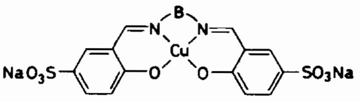
Introduction

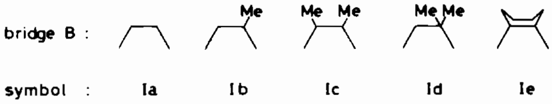
It has been repeatedly proposed [1–3] that metal substitution in metal chelates with multidentate ligands proceeds through dinuclear intermediates in which the ligand is partially bound to the leaving as well as to the incoming metal. It is obviously difficult to decide as to what the rate determining step is within the series of consecutive steps of bond cleavage and bond formation. Recently it was shown [1] for the metal exchange between various zinc polyamino-polycarboxylate complexes and Cu^{2+} that this question depends on the ligation capacity of the ligand.

The present study on the kinetics of isotopic copper exchange in various Cu(salen) complexes (salen = dianion of bis-salicylaldehydeethylenediamine) was undertaken to contribute to the question of dinuclear intermediate formation with a rather specific model system: (i) Cu(salen) can form di- and even trinuclear adducts with Ni^{2+} and Cu^{2+} via the lone electron pairs of the phenolic oxygen [4, 5]; (ii) the copper for copper exchange, *i.e.*, *isotopic* metal substitution, has the advantage of leading to a dinuclear intermediate with two equivalent copper ions; (iii) the planar tetradentate ligand 'salen' is very symmetrical around the C–C bond of the ethylene diamine; therefore, the introduction of alkyl groups at the ethylene bridge of the ligand should be reflected kinetically if rotation around this bridge is involved in dinuclear intermediate formation.

Cu(salen) is insoluble in water; to obtain solubility the ligand was sulfonated in 5-position of the two salicylaldehyde rings. The sodium salt of this disulfonic acid 'S-salen' is well soluble in water and so are the corresponding complex Cu(S-salen) = *Ia* and its alkylated derivatives.



I = Cu(S-salen)



The reaction studied was the isotopic metal exchange between Cu(S-salen) and ^{64}Cu-labelled Cu^{2+} ions:

$$\mathrm{Cu(S\text{-}salen)} + {}^{*}\mathrm{Cu}^{2+} \rightleftharpoons {}^{*}\mathrm{Cu(S\text{-}salen)} + \mathrm{Cu}^{2+} \quad (1)$$

The variation in B consisted in the stepwise introduction of methyl groups and of the cyclohexane ring as shown for *Ia*–*Ie*.

Experimental

The complexes were prepared by condensation of 1,2-diaminoethane (or the corresponding diamines for *Ib*–*Ie*) with 2 mol of the sodium salt of salicylaldehyde-5-sulfonic acid (synthesized by a standard procedure [6]) in the presence of copper(II) acetate. The complexes were characterized by elemental analysis (see Table I). They contained varying amounts of crystal water, which is typical of sulfonates. The water content was determined by weight loss determination after vacuum heating and by Karl Fischer titration.

The various diamines were commercial except for racemic 2,3-diamino-butane applied for *Ic*, which was synthesized by reduction of diacetyl dioxime as described in the literature [7]. For the preparation of *Ie*

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TABLE I. Analytical Data.

Cu(S-salen)·xH_2O	MW	% Calculated				% Found			
		C	H	N	Cu	C	H	N	Cu
Ia·$3H_2O$	588.0	32.69	3.09	4.77	10.81	32.80	3.10	4.80	10.40
Ib·$2.5H_2O$	593.0	34.43	3.23	4.72	10.72	34.50	3.28	4.81	9.85
Ic·$2.5H_2O$	607.0	35.62	3.49	4.62	10.47	35.80	3.54	4.94	10.00
Id·$3H_2O$	616.0	35.10	3.60	4.55	10.32	35.40	3.78	5.10	9.74
Ie·$3.5H_2O$	651.1	36.90	3.87	4.30	9.76	36.80	3.90	4.70	9.60

the *cis*-isomer of 1,2-diamino-cyclohexane was used; it was separated from the *trans*-isomer present in the commercial product by a standard procedure [8].

The radioactive copper-64 was obtained by thermal neutron irradiation of copper nitrate (TRIGA-Forschungsreaktor, Institut für Kernchemie, Universität Mainz).

The exchange experiments were carried out in non-buffered aqueous solution, standardized by constant ionic strength (I = 0.5 *M* $NaNO_3$) and proton concentration (pH = 4), mostly at 80 °C. Monitoring was done by two-fold extraction of the Cu^{2+} ions with TTA (= thenoyltrifluoroacetone) into CH_2Cl_2 and CCl_4, followed by scintillation counting (NaI-crystal) of the residual aqueous phase. The rate of exchange, R_{ex}, was derived from the slope of McKay plots [9].

Results and Discussion

Cu(salen) is a thermodynamically very stable and kinetically rather inert complex, which is reflected by the results of isotopic copper exchange studies in pyridine [10] and in chloroform [11] as solvent, *e.g.*

Kinetic inertness towards copper exchange is also observed for the disulfonated complex Cu(S-salen) = *I* when studied in aqueous solution. In the present investigation most of the runs had to be done at 80 °C to obtain decent rates. Since the ligand S-salen is a Schiff base it was considered necessary to prove the stability of complexes *Ia–Ie* towards hydrolysis under the extreme conditions of the exchange studies, *i.e.*, for 24 hours at 80 °C and at pH = 4. The Vis-spectra showed that after this treatment decomposition is negligible.

It follows from Fig. 1(a) that under standard conditions (pH = 4, I = 0.5 *M*) the rate of exchange, R_{ex}, is proportional to the concentration of Cu(S-salen). The deviations from slope 1.0 in this logarithmic plot are practically within the limits of error. Fig. 1(b) demonstrates that at constant concentration of Cu(S-salen) the rate of exchange is also first order in the concentration of Cu^{2+} ions. The experimental rate law is, therefore:

$$R_{ex} = k \cdot [\mathrm{Cu(S\text{-}salen)}][\mathrm{Cu}^{2+}] \qquad (2)$$

The values for k as resulting from the data in Fig. 1 by least squares fitting are compiled in Table II. The error in k is approximately 5–10%. The comparatively fast reaction with *Ia* was studied at 50 °C instead of 80 °C. From its temperature dependence in the range 40 °C–70 °C an activation energy of 89.9 kJ/mol was obtained which allowed an extrapolation of k to 80 °C.

It is well-known that the kinetics of metal exchange reactions are subject to pH changes [1]. Although the present study was mainly undertaken to compare the reactivity of differently alkylated Cu(S-salen) complexes at constant pH, the pH dependence of reaction (1) with Cu(S-salen) = *Ia* was studied in some detail in the pH range 5.5–3.1. The result was a continuous decrease in k with increasing H^+ concentration, however, not proportional to $[H^+]^{-1}$ but proportional to $[H^+]^{-0.5}$. This surprising finding would reflect that $Cu(OH)^+$ or higher hydrolyzed species like $Cu_2(OH)_2^{2+}$ are not the reacting species in an associative reaction mechanism as suggested by rate law (2). On the other hand, the fact [12] that the copper exchange of the complex Cu(S-salphen) (= *I* with B = *o*-phenylenediamine instead of ethylenediamine as in *Ia*) is practically independent of pH changes between 4.5 and 2.5 suggests strongly that the observed rate reducing effect of protons is caused by an interaction of H^+ or OH^- with Cu(S-salen) and not with Cu^{2+} ions.

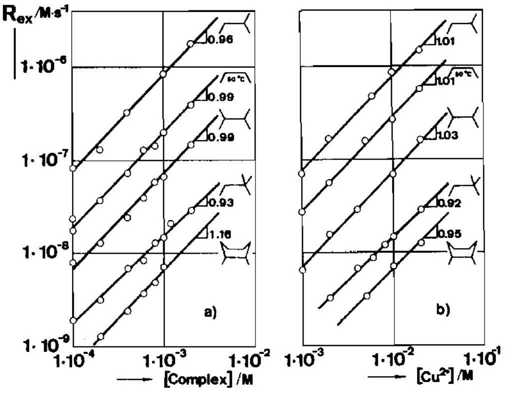
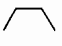
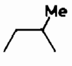
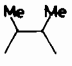
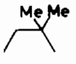


Fig. 1. Rate of exchange at 80 °C and pH = 4 (I = 0.5 *M*) as a function of complex concentration (see a; $[Cu^{2+}] = 10^{-2}$ *M*) and copper nitrate concentration (see b; [Cu(S-salen)] = 10^{-3} *M*).

As to be expected for the reaction between an anion (Cu(S-salen) with two $-SO_3^-$ groups) and a cation (Cu^{2+}), k decreases with increasing ionic strength ($NaNO_3$; 0.0035 to 0.014 *M*). The plot of log k *versus* $(I)^{1/2}$ has a slope of –5.5. On the basis of non-hydrolyzed Cu^{2+} ions being the cationic partner an anionic partner with a theoretical charge of –2.75 is derived from this slope. This could possibly point to the participation of Cu(S-salen) hydroxo species (OH^- probably attached to the copper) as reaction partner, a suggestion that is in qualitative agreement with the observed pH effects. On the other hand one has to be aware of the simplifying assumption used in the theoretical treatment of ionic strength effects on rate, namely; that the reacting species are charged hard spheres. This condition is definitely not fulfilled by the large and flat dianion Cu(S-salen).

The most interesting result of the present studies is the finding that under standardized conditions of pH, ionic strength and temperature there are large differences in the rate of metal substitution for complexes *Ia–Ie*. More specific, there is a surprisingly

TABLE II. Rate Constants at 80 °C (pH = 4; I = 0.5 *M*).

Complex	Bridge B	k/M^{-1} s^{-1}		k/M^{-1} s^{-1}	$\frac{k(Ia)}{k(Ix)}$
		From data in Fig. 1a	From data in Fig. 1b		
Ia		1.92×10^{-2} [a]	2.27×10^{-2} [a]	2.09×10^{-2} [a] 3.56×10^{-1} [b]	1
Ib		8.89×10^{-2}	7.38×10^{-2}	8.14×10^{-2}	4.4
Ic		7.38×10^{-3}	8.01×10^{-3}	7.70×10^{-3}	46
Id		1.47×10^{-3}	1.39×10^{-3}	1.43×10^{-3}	249
Ie		7.10×10^{-4}	5.97×10^{-4}	6.54×10^{-4}	544

[a] k at 50 °C. [b] k at 80 °C, obtained by extrapolation with $E_a = 89.9 \pm 3.5$ kJ mol^{-1}.

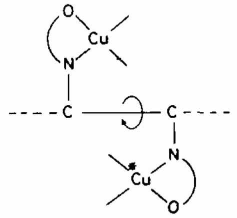
strong decrease in rate caused by methyl groups attached to the ethylene bridge. As far as the *number* of methyl groups is concerned the retarding effect is not additive in character but rather exponential in the sense that the effect of the *second* methyl group is stronger (see *Ia* → *Ib* → *Ic*) or even much stronger (see *Ia* → *Ib* → *Id*) than the effect of the *first* one. Two methyl groups at the same carbon atom reduce the rate by a factor of 249 (see *Id*); this very drastic effect is exceeded only by the *cis*-cyclohexane ring as bridge (see *Ie*).

It is well-known that transition metal complexes of salen can form adducts with metal ions [4, 5], the second metal being coordinated to the oxygen atoms of the ligand. Therefore, it is reasonable to assume that in reaction (1) the $^*Cu^{2+}$ ion approaches the complex on the oxygen side. If so, the observed rate effects of methyl groups at the ethylene bridge (*i.e.*, on the *nitrogen* side) are steric *not* in the sense of *shielding*, but in the sense of *remote* steric hindrance. The fact that retardation is strongest for *Ie* with the cyclohexane ring and also very strong for 2 methyl groups at the same carbon atom suggests that the reduction in rate is due to more or less hindered C–C bond rotation in the ethylene bridge. Such a rotation seems to be necessary for the formation of the intermediate which – in agreement with the experimental rate law (2) – is made up of the complex (possibly hydroxylated) and of the hydrated Cu^{2+} ion.

The very slow copper exchange between Cu(S-salen) and Cu^{2+} is governed by the 'associative' rate term k[Cu(S-salen)][Cu^{2+}]. Cu(S-salen) has no 'free' ligation capacity available so that stable intermediate mixed complexes like [Cu(S-salen)·Cu^{2+}] cannot be formed in aqueous solution, which is in agreement with the observed first order dependence in Cu^{2+} ions up to [Cu^{2+}]/[Cu(S-salen)] = 20.

It is obvious that the coordination of the incoming Cu^{2+} by Cu(S-salen) becomes possible only when part of the occupied donor capacity of salen in Cu(S-salen) is set free. Since salen is a highly 'symmetrical' ligand it is plausible to assume that this occurs by Cu–O and (more or less simultaneous) Cu–N bond rupture, so that one of the two sets of $\overset{\frown}{\text{N O}}$ donor pairs of salen becomes available. The data compiled in Table II are very essential in the sense that they prove another energy barrier (in addition to that for bond cleavage) to be relevant, namely the barrier to bring the free $\overset{\frown}{\text{N O}}$ donor pair into a proper orientation for the incoming Cu^{2+} ion. Looking at a model of Cu(S-salen) one learns that rotation around the C–C bond of the ethylene bridge seems to be necessary to achieve this. It is obvious that methyl groups at the carbons of the ethylene higher bridge hinder this rotation.

It follows that the geometry of the transition state could be such that the leaving and entering copper is located above and below the CuN_2O_2 coordination plane of the ground state, each being 'half bound' to one of the two sets of $\overset{\frown}{\text{N O}}$ donor pairs:



CuN_2O_2 plane of Cu(S-salen) in the ground state

This drawing is schematic, especially in the sense that the degree of rotation necessary for bonding of the incoming copper is probably much smaller than shown in the drawing. The steric effect of the methyl groups is the hindrance between these and the other half of the complex upon rotation. On the basis of this interpretation it makes sense that complex *Ie* is the slowest because of its rather rigid bridge.

The question of what the rate determining step is in copper for copper substitution in Cu(S-salen) can be answered in the following way. Since the formation of a symmetrical dinuclear intermediate is involved the cleavage of one Cu–O and one Cu–N bond *as well as* the proper orientation of the ligand for the incoming copper represent the highest energy barrier. This orientation is obviously associated with a rotation around the C–C bond of the ethylene bridge and contributes significantly to the entropy and enthalpy of activation. The determination of the single $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values is in progress.

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