

Polarographic Studies of Mixed Ligand Complexes of Copper Cadaverine with Some Carboxylic Acids

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Mixed ligand complexes of Cu(II) with cadaverine and carboxylic acids including adipic acid, succinic acid, maleic acid, malonic acid and phthalic acid have been studied polarographically. Formation constants of these complexes have been evaluated using McMaster and Schaap technique. The log K values for Cu-Cdv-Phth, Cu-Cdv-Mal, Cu-Cdv-Malo, Cu-Cdv-Succ and Cu-Cdv-Adp systems are -3.02, -3.50, -3.11, -3.67 and -2.51, respectively. The pH's of the solutions were kept at 7.9, 8.6, 8.2, 8.3 and 8.2 for the Malo-Cdv, Mal-Cdv, Adp-Cdv, Succ-Cdv, Phth-Cdv systems, respectively.

INTRODUCTION

Mixed ligand complexes are formed in solution containing metal ions with two or more different ligands. The investigations on mixed-ligand complexes have been stimulated due to their analytical applications, their formation as intermediates in ligand displacement reactions as well as in metal and enzyme catalysed reactions and their possible significance as model for biological process.¹⁻⁶ Mixed ligand complexes have been widely studied and a number of reviews have appeared on their stabilities, the kinetics of ligand interactions, structural isomerism and analytical applications of certain types of reactions.² The formation of ternary complexes between copper(II) and various ligands have received intermittent attention over a number of years. The exchangeable portion of Cu(II) in blood plasma occurs mainly through the mixed ligand complexes. Sarkar and Kruck⁷ have reported the separation of a mixed ligand complex Cu (histidine) (threoninate) from normal human serum and have detected mixed ligand complex Cu(histidinate)(seriate) and Cu(histidine)(threoninate) in solution prepared at physiological pH. Khurana *et al.*⁸ have obtained the formation constants of mixed chelates of Cu(II) with oxalate, malonate, maleate or tartarate. However, during the present investigations, the ligand displacement technique in which a more strong complexing species is added to mixture of a metal ion with a weaker complexing species has been studied. We have used cadaverine as the stronger ligand and carboxylic acids as the weaker ligands.

EXPERIMENTAL

All the chemicals used were of AR grade. Cadaverine and sodium salts of adipic acid, succinic acid, maleic acid, malonic acid and phthalic acid were used as complexing agents. Stock solution (M/40) of Cu(II) was prepared by dissolving copper nitrate in double distilled water and estimated volumetrically. The ionic strength was maintained at 1.0 M with sodium perchlorate in all systems. The pK values of all ligands were determined by the method of Elbert and Serjeant. A 0.002% triton-x-100 was used in each solution of ligands under study in order to suppress maxima. Throughout the measurements purified nitrogen gas pre-saturated with the given mixture was passed for 35 minutes to remove dissolved oxygen. Current-voltage measurements were made on a manual polarograph using a potentiometer (OSAW slide wire potentiometer) and galvanometer (AJCO, Model No., P-G1, Sr. No. P 71049). The sensitivity of the polarograph used for current voltage curves was $3.7 \times 10^{-2} \mu\text{a/div}$.

In the open circuit at 50 cm mercury height the capillary used has $m = 1.28 \text{ mg sec}^{-1}$ and $t = 3.0 \text{ sec}$.

The pH of the solution was measured with CD Century digital pH-meter. The pH's of all the solutions were adjusted to the desired value by adding either perchloric acid or sodium hydroxide solution. All the observations were made at $25 \pm 1 \text{ symbol}^\circ\text{C}$. The solution was placed in a H-type cell coupled with a saturated calomel electrode through an agar-agar (saturated with sodium chloride salt bridge). The resistance of the cell was more than 200 ohm, IR drop correction was made by L.P. conductoscope (024).

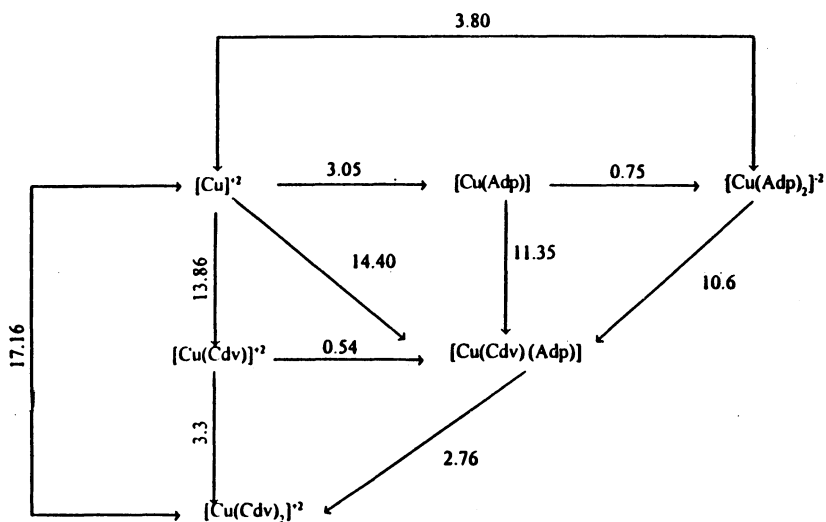
RESULTS AND DISCUSSION

In all cases Cu(II) reduction was found to be reversible by analysis of the slope of the plots of $\log \frac{i}{i_d - i}$ vs. Ed.e.

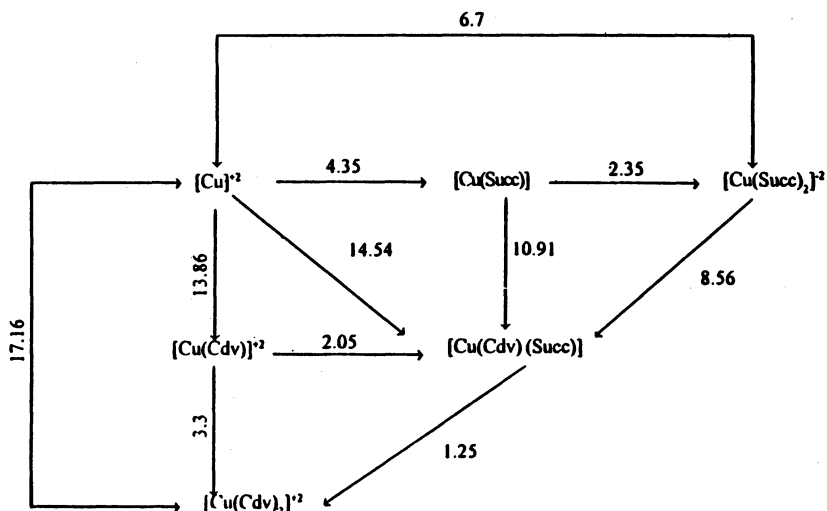
A well defined polarographic wave was obtained in all the systems. Plots of i_d vs. $i_{\text{eff}}^{1/2}$ were found to be linear and passed through the origin showing that the reduction is diffusion controlled. The plots of $\log \frac{i}{i_d - i}$ vs. Ed.e. were also linear with a slope of $31 \pm 2 \text{ mv}$. Thus the electrode processes are reversible (involving 2 electrons) and the current was limited by diffusion. The half wave potential were obtained from the zero intercept of plots $\log \frac{i}{i_d - i}$ vs. Ed.e. The $E_{1/2}$ of Cu(II) at ionic strength 1.0 (NaClO_4) was +0.0015 volts vs. S.C.E. (the shift in $E_{1/2}$ to more negative potential with increase in Cdv was observed in all cases). The shift is greater in the presence of weaker ligands. It signifies the formation of mixed ligand complex. The plot of $E_{1/2}$ vs. $-\log [X]$ yielded a smooth curve for every system with the presence of more than one complex species in this medium. Hence the Schaap-McMaster's⁹ treatment was applied and F_{10} functions have been evaluated. The values of A, B and C were computed by graphical extrapolation method as proposed by Leden.¹⁰ The method of Deford and Hume¹¹ was used to calculate the complex formed.

The values of $E_{1/2}$, $\log I_M/I_C$ and $F_{10}(XY)$ are given in Table-6 for Cu-Cdv-Adp system and similar trends found in other systems. The functions $F_{10}[X, Y]$ vs. concentration of variable ligand ion $[X]$ have been plotted, where $X =$ cadaverine. The values of A were calculated from stability constant of Cu(II)-Y species (where $Y =$ adipic, succinic, maleic, malonic or phthalic acid using the relation:

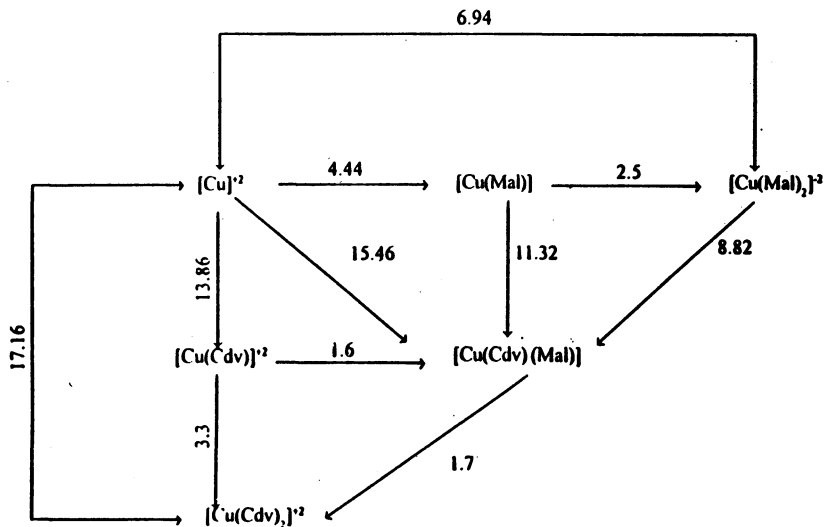
$$A = 1 + \beta_{01}[Y] + \beta_{02}[Y]^2$$



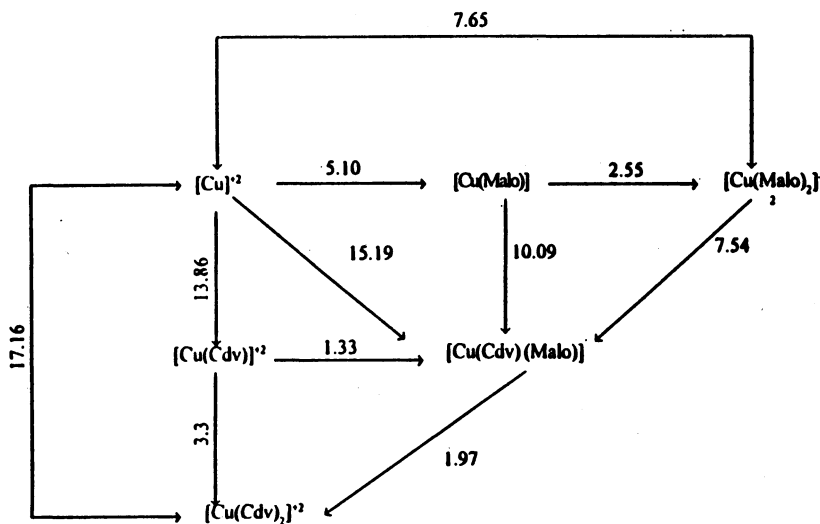
Scheme No. 1 Complex equilibria in Cu(II)-Cadaverine-Adipate system



Scheme No. 2 Complex equilibria in Cu(II)-Cadaverine-Succinate system



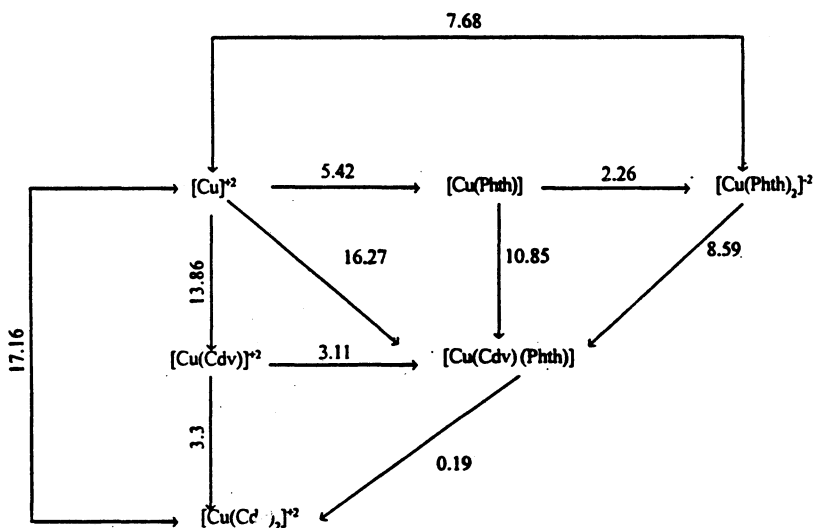
Scheme No. 3 Complex equilibria in Cu(II)-Cadaverine-Maleate system



Scheme No. 4 Complex equilibria in Cu(II)-Cadaverine-Malonate system

The intercepts at $X = 0$ of the plots of $F_{00}[XY]$, $F_{10}[XY]$ and $F_{20}[XY]$ vs. $[X]$ give the respective values of A, B and C. The values of A obtained graphically are identical to the calculated values. The values of β_{11} were calculated from the value of B using the relation:

$$B = \beta_{10} + \beta_{11}[Y]$$



Scheme No. 5 Complex equilibria in Cu(II)-Cadaverine-Phthalate system

The values of C show that they agree with β_{20} values of binary complex. The results for Cu-Cdv-Adp, Cu-Cdv-Succ, Cu-Cdv-Mal, Cu-Cdv-Malo and Cu-Cdv-Phth are summarised in the schemes 1–5.

Various observations can be made. The tendency of Cu(phthalate), Cu(malonate), Cu(maleate), Cu(succinate) or Cu(adipate) and $\text{Cu}(\text{Cdv})^{2+}$ to add a second ligand can also be compared. The log K values are (2.20, 2.31), (2.24, 2.42), (2.44, 2.79), (2.44, 2.79), (2.41, 2.05) and (0.92, 2.41), respectively for the addition of phthalate, malonate, maleate, succinate and adipate. The tendency to add $[\text{Cdv}]$ to $[\text{Cu}(\text{phthalate})]$ and $[\text{Cu}(\text{Cdv})]^{2+}$, $[\text{Cu}(\text{malonate})]$ to $[\text{Cu}(\text{Cdv})]^{2+}$ and $[\text{Cu}(\text{maleate})]$ to $[\text{Cu}(\text{Cdv})]^{2+}$ and $[\text{Cu}(\text{succinate})]$ to $[\text{Cu}(\text{Cdv})]^{2+}$ and $[\text{Cu}(\text{adipate})]$ to $[\text{Cu}(\text{Cdv})]^{2+}$ can also be compared and the observed log K values are (9.92, 3.86), (10.36, 3.59), (11.32, 3.82), (10.91, 3.56) and (12.15, 3.46) for Cdv-Phth, Cdv-Malo, Cdv-Mal, Cdv-Succ and Cdv-Adp systems respectively.

TABLE-1
pK VALUE OF LIGANDS AT 25°C

S.No.	Ligands	pK ₁	pK ₂
1.	Cadaverine (Cdv)	11.85	10.76
2.	Adipic acid	4.04	5.33
3.	Phthalic acid	2.90	5.40
4.	Succinic acid	4.17	5.48
5.	Malonic acid	2.83	5.61
6.	Maleic acid	1.90	6.24

TABLE-2
OVERALL STABILITY CONSTANTS OF Cu(II) COMPLEXES

System	log β_1	log β_2
Cu(II)-Cdv	13.86	17.16
Cu(II)-Adp	3.05	3.80
Cu(II)-Succ	4.35	6.70
Cu(II)-Mal	4.44	6.94
Cu(II)-Malo	5.10	7.65
Cu(II)-Phth	5.42	7.68

TABLE-3
THE OBSERVED log K VALUES

S.No.	Ligand	log K
1.	Cu(phthalate)	(2.20, 2.31)
2.	Cu(malonate)	(2.24, 2.42)
3.	Cu(Succinate)	(2.44, 2.79)
4.	Cu(adipate)	(2.44, 2.79)
5.	Cu(maleate)	(2.41, 2.05)
6.	Cu(Cdv) ²⁺	(0.92, 2.41)

Formation of mixed ligand complexes are favoured due to statistical factors possible charge neutralization, bonding inter molecular stacking, removal of steric hindrance in one of the binary parent complexes, etc. Sakurai *et al.*¹² have indicated that intra-molecular electrostatic interaction present in ternary species can stabilize them under favourable conditions. The mixed ligand stabilization constant log X_{11} is calculated from the disproportionation reaction as shown below:



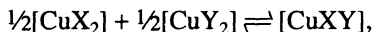
$$X_{11} = \frac{[\text{CuXY}]^2}{[\text{CuX}_2][\text{CuY}_2]}$$

The log X_{11} value greater than 0.6 indicated favoured formation of the mixed-ligand complexes over binary complexes. The high X_{11} values listed in Table-4 show that all these mixed ligand complexes are highly favoured.

TABLE-4
VALUES OF log X_{rs}

S.No.	Ternary system	log X_{11}
1.	Cu(II)-Cdv-Adp.	7.84
2.	Cu(II)-Cdv-Succ.	5.22
3.	Cu(II)-Cdv-Malo.	6.28
4.	Cu(II)-Cdv-Mal.	6.11
5.	Cu(II)-Cdv-Phth.	7.69

The stability of the mixed ligand complexes can also be compared with the binary complexes through K_M , K_S and $\log K$. The dimensionless mixing constant K_M for the formation of mixed complex:



where X is cadaverine and Y is phthalic, malonic, maleic, succinic or adipic acid showed the relative stability of the mixed complex in solution as compared to the parent binary complexes which is expressed in the form:

$$K_M = \frac{\beta_{11}}{\sqrt{\beta_{02}\beta_{20}}}$$

Hence, $\log K_M = \log \beta_{11} - \frac{1}{2}(\log \beta_{02} + \log \beta_{20})$

The statistical value of $\log K_M$ is $> (0.3)$. The stabilisation constant of K_S is therefore expressed in the form: $\log K_S = \log K_M - 0.3$.

The stabilization constant measures the extra-stability of the mixed complex, due to electrostatic forces and steric factors.

The positive values of mixing constant and stabilization constant show that ternary complexes are more stable than the binary complexes. The positive values of stabilization constant have also been observed by many workers in the past. The observed values of $\log K_M$ and $\log K_S$ are reported in Table 5.

TABLE-5
COMPLEX FORMATION CONSTANTS FOR THE
MIXED LIGAND COMPLEXES AT 25X ($\mu = 1.0$)

S.No.	Mixed ligand complex	$\log K_M$	$\log K_S$
1.	Cu(II)-Cdv-Adp.	3.92	3.62
2.	Cu(II)-Cdv-Succi	2.61	2.31
3.	Cu(II)-Cdv-Malo.	3.14	2.84
4.	Cu(II)-Cdv-Mal.	3.05	2.76
5.	Cu(II)-Cdv-Phth.	3.85	3.55

The $\log K$ values for Cu-Cdv-Phth, Cu-Cdv-Malo, Cu-Cdv-Mal, Cu-Cdv-Succ, and Cu-Cdv-Adp systems are (-3.02) , (-3.50) , (-3.11) , (-3.67) and (-2.51) , respectively.

In polarographic investigations, the value of $\log \beta_1$ is evaluated by DeFord and Hume method.¹¹ The values of $\log \beta_1$ obtained by DeFord and Hume method contain higher uncertainty than in $\log \beta_2$ values. Similarly there exists some uncertainty in the values of $\log \beta_{11}$ also as calculated by the method of Schaap and McMaster.⁹

Hence the values of $\log K$ calculated from the $\log \beta_1$ and $\log \beta_{11}$ values may include considerable uncertainties. Sigel¹² has also reported that as far as possible, $\log X (= Z \log K_M)$ should be used for the estimation of stability of unknown mixed-ligand complex because differences between the two systems are usually more significant.

TABLE-6
Cu(II)-CADAVERINE-ADIPATE SYSTEM

$E_{1/2}$ Cu(II) = + 0.015 volts vs. S.C.E.

Concentration of ligand Y (Adipate) = 0.20 M, $I_s = 4.7992 \mu\text{A}$

S.No.	$[X] \times 10^2$	$\log \frac{I_s}{I_c}$	$\Delta E_{1/2}$ volts	$F_{00}[X] \times 10^{-11}$	$F_{10}[X] \times 10^{-14}$	$F_{20}[X] \times 10^{-16}$
1.	0.580	0.0186	0.3461	31.1454	5.3699	3.655
2.	1.160	0.0241	0.3626	86.8680	7.4886	3.654
3.	1.740	0.0298	0.3844	167.1480	9.6062	3.653
4.	2.320	0.0314	0.3851	269.2740	11.6066	3.602
5.	2.900	0.0362	0.3884	401.8870	13.8582	3.658
6.	3.480	0.0376	0.3891	559.0040	16.0633	3.682
7.	4.060	0.0390	0.3899	734.4250	18.0893	3.655
8.	4.640	0.0399	0.3946	948.8686	20.4458	3.706
9.	5.220	0.0412	0.3971	1172.2663	22.4648	3.681

$A_{cal} = 2.244 \times 10^6$, $B = 3.25 \times 10^{14}$, $C_{av} = 3.6606 \times 10^{16}$

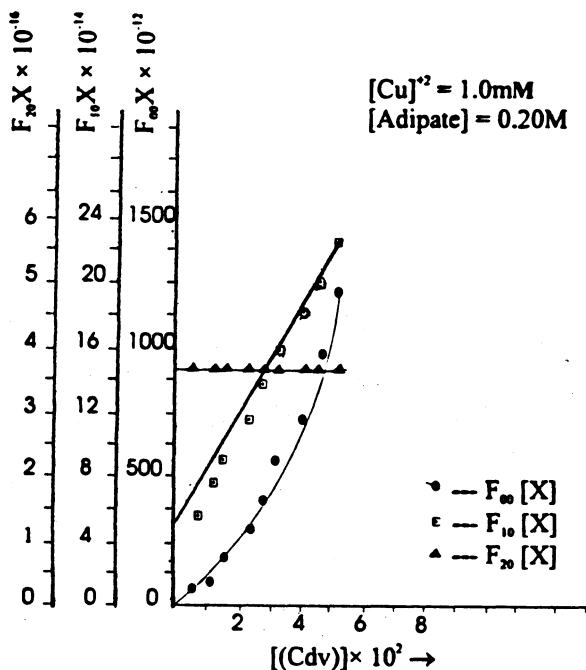


Fig. 1

TABLE-7
STABILITY CONSTANT PARAMETERS FOR MIXED LIGAND COMPLEXES AT 25X
($\mu = 1.0$)

S.No.	[X]	[Y]	A ($\times 10^6$)	B ($\times 10^{14}$)	C_{av} ($\times 10^{16}$)	β_{20} ($\times 10^{17}$)	$\log \beta_{11}$
1.	Cadaverine	Adipic acid	2.244	3.25	3.6606	1.445	14.40
2.	Cadaverine	Succinic acid	2.009	1.42	3.0477	1.445	14.54
3.	Cadaverine	Malonic acid	3.530	3.85	3.5375	1.445	15.19
4.	Cadaverine	Maleic acid	1.800	6.50	5.2640	1.445	15.46
5.	Cadaverine	Phthalic acid	1.967	3.76	3.9840	1.445	16.27

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REFERENCES

1. P.I. Ting and G.H. Nahcollas, *Inorg. Chem.*, **11**, 2414 (1972).
2. A.T. Pilipenko and M.M. Tanahaiko, *Talanta*, **21**, 501 (1974).
3. V.S. Sharma and J. Schubert, *Chem. Edu.*, **40**, 506 (1969).
4. H. Yoki, M. Otogiri and T.I. Sobe, *Bull. Chem. Soc. Jp.*, **44**, 2395 (1971).
5. P.V. Selvraj and M. Santappa, *J. Inorg. Nucl. Chem.* **38**, 837 (1976).
6. L. Hellerman and C.C. Stock, *J. Biol. Chem.*, **125**, 771 (1938).
7. T.P.A. Kruck and B. Sarkar, *Canad. J. Chem.*, **51**, 3555 (1973).
8. S.C. Khurana and I.J. Nigam, *J. Inorg. Nucl. Chem.* **40**, 159 (1978).
9. W.B. Schaap and D.L. McMaster, *J. Am. Chem. Soc.*, **83**, 4699 (1961).
10. I. Leden, *Z. Phys. Chem.* **1888A**, 160 (1941).
11. D. DeFord and D.N. Hume, *J. Am. Chem. Soc.*, **73**, 5321 (1951).
12. H. Sigel, *Angew Chem.*, **14**, 394 (1975).

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