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Coordination Chemistry Reviews
190–192 (1999) 357–369

COORDINATION CHEMISTRY REVIEWS

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Chiral metal complexes as probes in electron-transfer reactions involving metalloproteins

Klaus Bernauer *, Simona Ghizdavu, Luca Verardo

Institut de Chimie, Université de Neuchâtel, Avenue de Bellevaux 51, 2000 Neuchâtel, Switzerland

Accepted 13 March 1999

Contents

Abstract

Chiral recognition in electron-transfer reactions between metalloproteins and optically active, low molecular weight coordination compounds is well established. In the case of the blue copper proteins plastocyanin and azurin inner- and outer-sphere reactions can be distinguished by electron-transfer mediated binding of the product complexes to the protein. For inner-sphere reactions the exact reactive site can be identified by this technique. Individual activation parameters for both reaction pathways are determined, in part as a function of pH. The selection of pathways, which not only depends on the reaction conditions and the chemical nature of the reagents but also on their chirality, is strongly influenced by site directed mutations provided that the latter take place near the reactive site. Molecular modelling suggests that the enantioselectivity of the inner-sphere reactions might be due to hydrogen bonding as well as to nonbonding stereo effects.

Keywords: Metalloproteins; Electron transfer; Chiral metal complexes; Stereoselectivity; Site selection

* Corresponding author. Tel.: +41-32-7182485; fax: +41-32-7182511.
E-mail address: klaus.bernauer@ich.unine.ch (K. Bernauer)

0010-8545/99/$ - see front matter
PII: S0010-8545(99)00094-6

1. Introduction

Stereoselectivity in electron-transfer reactions between low molecular weight coordination compounds was described for the first time in 1980 [1]. Since then interest in reactions using electron transfer as model reactions for chiral recognition rapidly increased and the field has been extensively reviewed [2–4]. In general the reactions are considered to be of the outer-sphere type and either ion-pair formation or hydrogen bonding are thought to be responsible for the observed selectivity. Nevertheless, some examples of selective inner-sphere reactions have been described [5–11] and it has recently been shown that even in the absence of ion-pair formation or hydrogen bonding simple stereo effects can give rise to substantial stereoselectivity [12,13]. An early attempt to demonstrate chiral recognition in an electron-transfer reaction involving metalloproteins failed, racemic and optically active $[Co(en)_3]^{3+}$ showed identical reaction rates for the oxidation of plant ferredoxin [14]. The first example of stereoselective electron transfer, reported in 1988, was observed in the reduction of plastocyanin by optically active Fe^{II} complexes [15]. Since then several cases were described for various metalloproteins such as plastocyanin [3,16], plant ferredoxin [17], cytochrome c [18–23], and superoxide dismutase [24] which were reacted with different chiral metal complexes. Chiral recognition has also been observed in electron-transfer reactions between metalloproteins and a non-metallic reagent [25].

Experimental determination of kinetic stereoselectivity can be carried out by two different techniques, either by measuring the reaction rate with both enantiomers separately, or by using a racemic reagent and determining the enantiomeric excess of the reagent or the product, during or at the end of the reaction. This latter technique can only be used if the reagent forms an inert compound in at least one of the two oxidation states involved. The procedure is especially useful for reagents for which racemization is too fast to allow the use of individual enantiomers but sufficiently slow compared to the rate of the observed reaction. An interesting example recently described is the selective quenching of the fluorescence of Tris–diimine complexes of Eu^{III} or Tb^{III} by ferricytochrome *c* [26]. On the other hand, in cases where both oxidation states, that of the reagent and that of the product are labile, only the use of ligands forming complexes with a unique structure and predetermined chirality permit the discussion of observed stereoselectivity effects in terms of known structures.

In several redox systems involving metalloproteins stereoselectivity was determined as a function of temperature and isokinetic $\Delta H^{\#}/\Delta S^{\#}$-relationships between diastereoisomeric couples were found [3]. The differences in the activation parameters, while rather small in general, sometimes reach surprisingly high values; some typical examples are shown in Table 1. The question therefore arises, whether or not such large differences could be the result of different reaction pathways and/or reaction mechanisms.

A useful technique to identify electron transfer sites in inner-sphere reactions is the use of reagents like Cr^{2+}, which form inert reaction products and therefore

Table 1
Differences of the activation parameters between enantiomers in some electron-transfer reactions involving metalloproteins

Protein	Reagent[a]	$\Delta\Delta H^{\neq}_{\Lambda-\Delta}$ (kJ mol^{-1})	$\Delta\Delta S^{\neq}_{\Lambda-\Delta}$ (J K^{-1} mol^{-1})	Ref.
Plastocyanin	[Co^{II}(alamp)]	16.1	55	[27]
Azurin	[Fe^{II}(promp)]	−5.6	−18	[28]
	[Co^{II}(promp)]	−7.6	−24	[28]
Plant Ferredoxin	[Co^{III}(alamp)(py)][1]	−11.8	−38	[17]

[a] For the definition of abbreviations see text, Section 2.

remain attached to the site used for electron transfer [29]. This technique has also been applied to metalloproteins, but identification of the exact structure of the reaction products proved to be difficult [30,31]. We have recently shown, by applying this technique to the reaction between plastocyanin and optically active Co^{II} complexes, that the large difference observed in the activation parameters between enantiomers is due, at least in part, to the selection of different reactive sites [27,32,33]. On the basis of these observations we presume that large differences in the activation parameters of enantiomeric reagents might be a sign of multiple-site electron transfer, even in reactions where the mechanisms can not be differentiated experimentally, e.g. with the entirely labile $Fe^{III/II}$ system or with inert complexes reacting exclusively by outer-sphere pathways. In the following we would like to illustrate, based on previous and some new results obtained with the blue copper proteins plastocyanin and azurin[1], which kind of information can be obtained from selectivity measurements by using metal complexes with predetermined chirality as low molecular weight electron-transfer agents.

2. Redox active metal complexes with predetermined chirality

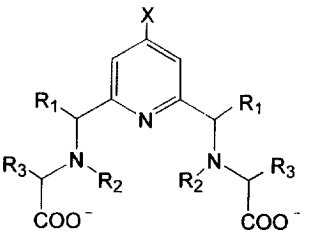
As mentioned in the Section 1, metal complexes as electron-transfer reagents used in stereoselectivity studies should occur as a single compound with definite structure and chirality. For metal ions forming octahedral, inert compounds such as Co^{III}, Cr^{III}, Rh^{III}, this can easily be achieved by using isolated enantiopure isomers. These complexes may or may not contain optically active ligands. In the case of compounds containing labile metal centres, on the other hand, their chirality is only determined by that of the ligands. In general such compounds are present in an equilibrium mixture of different isomers and/or conformers. In order to achieve preferential formation of one single form to more than 98%, the selected isomer

[1] The data given in this work are obtained with wild type azurin prepared from *Ps. aeruginosa* expressed in *E. coli*.

must be about 10 kJ mol^{-1} more stable than all the others. Ligands of this type are called stereospecific. Since the pioneering work of Corey and Bailar [34] the structural conditions to realise stereospecificity are known and the stereospecific formation of 1:1 metal to ligand complexes was reviewed [35]. An up-to-date compilation of the structural requirements governing the stereochemistry of coordination compounds, including chirality, has recently been published [36]. However, the assertion of stereospecificity in the formation of labile coordination compounds in solution is always based on the characterisation of analogous compounds containing inert coordination centres and/or the determination of X-ray structures in the solid. As the determination of the relative presence of isomers in solution is an unsolved problem in most cases, there remains nevertheless some uncertainty about the real degree of specificity in such systems.

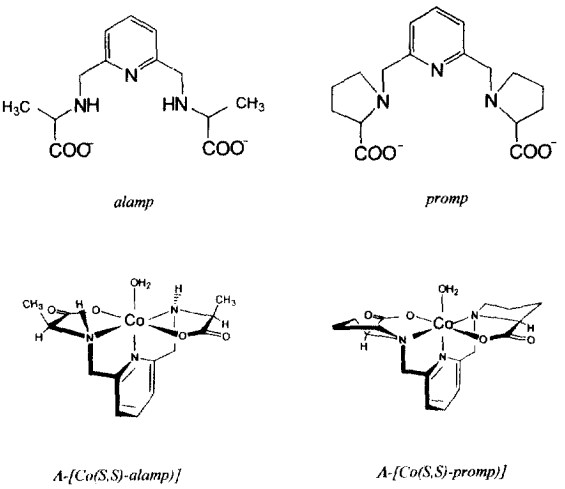
When we started our investigations of stereoselectivity in electron transfer reactions we developed a new group of stereospecific ligands, especially designed for this purpose, the basic framework of which is I [5,37]. The main reasons for the choice of the architecture of these ligands were:

- formation of octahedral complexes with one single C_2 symmetric geometrical arrangement due to the meridional coordination of the N⌒N⌒N and the facial arrangement of the two N⌒N⌒O moieties;
- numerous possibilities of introduction of chiral centres by R_1 and R_3 which by R_2 can be ring-closed;
- possibility of R_2 to allow either hydrogen bonding ($R_2 = H$) or the introduction of a new chiral centre on coordination (R_2 = alkyl);
- introduction of various -X as electron donating or electron withdrawing groups
- free sixth coordination site allowing the introduction of various electron conducting, monodentate ligands.



(I)

Several aspects of the electron-transfer reaction between type 1 copper proteins plastocyanin and azurin by the Co^{2+} complexes of the optically active ligands *N,N'*-[(pyridine-2,6-diyl)bis(methylene)]bis[(*R*)- or (*S*)-alanine], ((*R,R*)- or (*S,S*)-alamp), and *N,N'*-[(pyridine-2,6-diyl)bis(methylene)]bis[(*R*)- or (*S*)-proline], ((*R,R*)- or (*S,S*)-promp) will be discussed. The two ligands are considered to form metal complexes with predetermined chirality due to the more stable *exo*-position of the R_3 substituent. This position, also enforced in promp by the tetrahedral structure of the coordinated nitrogen atoms, yields Λ-configuration of the complexes with



Scheme 1.

ligands of (*S*,*S*)-chirality (Scheme 1). These two ligands have been selected for the hydrogen bonding ability of the former and their absence and the lower accessibility of the metal centre in the latter. Furthermore, as the complexes are uncharged, electrostatic effects can be disregarded.

3. Electron-transfer mediated binding of optically active Co^{III} complexes

Electron transfer between metalloproteins and Co^{2+} complexes can take place by two different mechanisms, inner-sphere when the Co^{III} species formed by the electron transfer remains attached to the protein and outer-sphere when the oxidation product appears as the free aqua species[2] according to Eqs. (1) and (2)[3]

$$Cu^{II}P^{n-} + [Co^{II}(L)(H_2O)] \leftrightarrows [(L)Co^{III}\text{-}PCu^{I}]^{n-} + H_2O \quad (1)$$

$$Cu^{II}P^{n-} + [Co^{II}(L)(H_2O)] \leftrightarrows Cu^{I}P^{(n+1)-} + [Co^{III}(L)(H_2O)]^{+} \quad (2)$$

where P is the apoprotein of plastocyanin or azurin.

The product obtained containing the bound Co^{III} species can then be reoxidized according to Eq. (3) and the spectroscopic and chiroptical properties compared to those of the initial protein.

[2] We call outer-sphere each reaction in which no Co^{III} is bound to the protein disregarding whether or not the metal center is coordinated to the protein surface in the transition state.

[3] The coordinated water molecule at the sixth coordination site of labile Co^{II} complexes, shown in Eqs. (1) and (2), is omitted in the following.

$$[(L)Co^{III}\text{-}PCu^{I}]^{n-} + [Fe(CN)_6]^{3-} \leftrightarrows [(L)Co^{III}\text{-}PCu^{II}]^{(n-1)-} + [Fe(CN)_6]^{4-} \quad (3)$$

Blue copper proteins are especially suitable for the evaluation of the reaction sequence by measurements of circular dichroism (CD). The proteins in the oxidized state and the Co^{III} complexes with either water or an imidazole molecule at the sixth coordination site have characteristic CD spectra [32]. On the other hand, the reduced protein has no CD signal in the visible spectrum. The CD spectra of the complete reaction sequences with both enantiomers of [Co(alamp)] are given in Fig. 1 for plastocyanin and azurin, respectively.

From the results given in Fig. 1 it is concluded by the identity of the CD spectra with the corresponding mixed ligand Co^{III} complexes with imidazole at the sixth coordination site that the oxidation product is completely or partially fixed on a histidine unit of the proteins. In the case of plastocyanin one of the two histidines forming the coordination site, must be involved, most likely His-87. The difference spectra of the reoxidized product clearly show that the initial coordination sphere of the copper centre can not be restored due to the coordination of His-87 to the cobalt centre. The fixation at this position is further confirmed by the influence of point mutations at position Leu-12 in the neighbourhood of His-87 in the 3D structure. Whereas only 40% of the native protein is bound to the Δ-[Co^{III}((*R*,*R*)-alamp]$^{+}$ unit after complete electron transfer, the reaction is entirely inner-sphere with the Leu12Gly mutant [38].

With azurin, on the other hand, the spectra corresponding to the contribution of the Cu chromophore to the CD spectra of the reoxidized proteins are almost perfectly superimposable for both enantiomers to the initial spectrum of the protein. The reaction therefore occurs not at a histidine coordinated to the copper centre but at one of the two extra histidines contained in azurin. As only one of them, His-83, is solvent exposed and accessible by the reagent it is likely that the entrance of the electron takes place at this remote position, at a distance of some 18–20 Å from the target redox centre.

4. Stereo- and site selection

According to the results given in Fig. 1, binding of the reagent, corresponding to the inner-sphere reaction, is only partial in the reported cases, in other words the reaction occurs to some extent by an outer-sphere mechanism as well. This allows the conclusion, that electron transfer involving chiral and non racemic reagents can take place at, at least two different sites, each of them exhibiting different enantioselectivity. Detailed measurements revealed that the selection of sites strongly depends on the nature of the ligands used, their substitution pattern and their chirality, as well as on the reaction conditions such as pH and temperature. Table 2 contains some significant values for the two proteins and the two reagents under comparable reaction conditions.

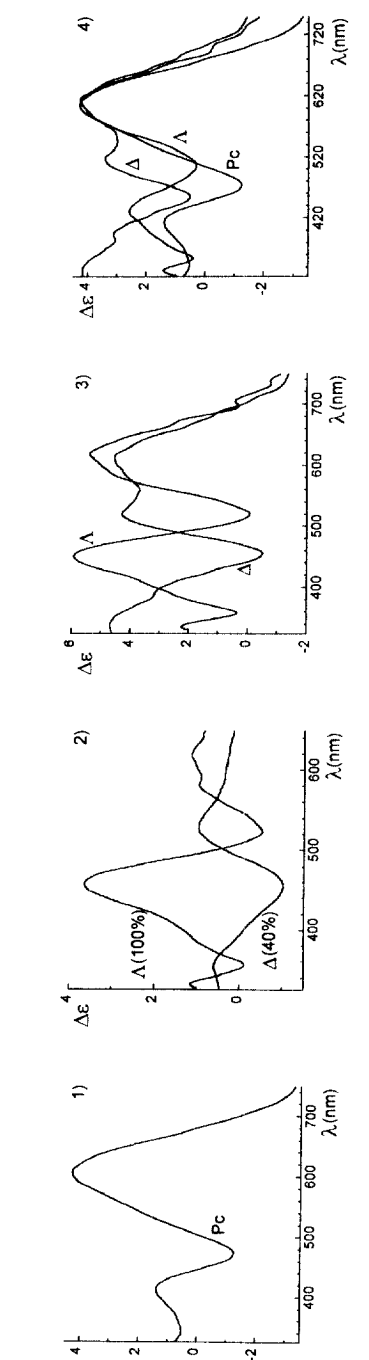


Fig. 1. CD spectra of the reaction sequence of Δ- and Λ-[Co(alamp)] with plastocyanin (A) and wt azurin (B): (1) oxidized protein; (2) after electron transfer and dialysis. Percentage values indicated give the amount (%, relative to the amount of the protein) of fixed Co^{III}, the spectra are identical to Δ-$[Co^{III}((R,R)$-alamp)(imidazole)$]^+$ and Λ-$[Co^{III}((S,S)$-alamp)(imidazole)$]^+$, respectively; (3) after reoxidation by $[Fe(CN)_6]^{3-}$ and dialysis; (4) difference spectra (2)–(3) superimposed on the initial spectrum (1). Reaction conditions: $T = 20°C$ (pc), 55°C (az); pH 7.0 (phosphate, 0.1 M).

The variation of the ligands allows the study of stereochemical interactions governing the selection of reaction pathways. The variation of the reaction conditions, such as pH, ionic strength, temperature and pressure, on the other hand, gives information about the influence of modifications on the protein surface and the surrounding reaction medium. The reagents used in this work are electrically neutral, hence, modifications of the overall charge of the protein by the protonation of solvent exposed groups and the ionic strength of the reaction medium are of minor influence only. Variation of the selection of pathways due to pH variations can therefore be explained as an influence on the precursor formation equilibrium.

In the case of plastocyanin we have shown that the part of the inner-sphere reaction with Δ-[Co((*S*,*S*)-alamp)] increases with increasing pH. This has been explained by the formation of an intermediate in which the two metal centres are linked together by the negatively charged imidazole moiety of His-87 [32]. With azurin the reaction presumably takes place at the uncoordinated His-83 and the influence of pH can be explained by the protonation of this group. The results for both enantiomers of [Co(promp)] and a pH range of 5–9, represented in Fig. 2, indicate that for this reagent the reaction mechanism changes from almost entirely outer-sphere at low pH to mainly inner-sphere in more basic solutions. The observation that the amount of bound complex increases in a nearly proportional way compared to the deprotonation of the imidazole group suggests that the simultaneously occuring outer-sphere reaction is pH independent.

Measurements of the temperature dependence of both, the global and the individual reaction rates of the two reaction modes offers the unique possibility to determine individual activation parameters of each of the two reaction pathways. Individual rate constants are calculated from the ratio of the reaction products of (1) and (2) assuming both being parallel reactions of the pseudo-first order type.

Table 2
Amount (%)[a] of chiral Co^{III} bound to blue copper proteins (relative to the total amount of protein) after electron transfer[b]

Protein	[Co(alamp)]		[Co(promp)]		Ref.
	Δ	Λ	Δ	Λ	
Plastocyanin					
Native	45	100	0	0	[27]
wt	50	100	0	0	[38]
leu12ala	75	100	0	0	[38]
leu12gly	100	100	0	0	[38]
Azurin					
wt[c]	61	40	5	17	This work

[a] Determined by the CD intensity after 8 half-lives of the electron-transfer reaction and the elimination of the excess [Co^{II}(L)] by dialysis; error limit ± 5%.

[b] pH 7.0 (phosphate); [protein] ca. 10^{-4} M; [Co^{II}(L)] = 10^{-3} M. T = 26°C.

[c] At 30°C.

Table 3
Individual activation parameters of the reduction of plastocyanin and azurin by optically active Co^{2+} complexes

Protein	$[Co^{II}(L)]$	pH	Inner-sphere			Outer-sphere		
			$\Delta H^{\neq}$ [a] (kJ mol^{-1})	$\Delta S^{\neq}$ [a] (J K^{-1} mol^{-1})	$\Delta G^{\neq}$ [b] (kJ mol^{-1})	$\Delta H^{\neq}$ [a] (kJ mol^{-1})	$\Delta S^{\neq}$ [a] J K^{-1} mol^{-1})	$\Delta G^{\neq}$ [b] (kJ mol^{-1})
Plastocyanin	Δ-[Co((*R*,*R*)-alamp)]	7.0	67.5	−24	74.4	45.9	−95	73.6
	Λ-[Co((*S*,*S*)-alamp)]	7.0	73.7	+5	72.7	Unknown[c]		
wt azurin	Δ-[Co((*R*,*R*)-promp)]	7.0	Not determined[d]			36	−133	74.5
		8.0	62	−64	80.7	33	−144	74.9
	Λ-[Co((*S*,*S*)-promp)]	7.0	63	−57	79.7	37	−129	74.8
		8.0	58	−65	77.0	33	−144	74.9
		9.0	52	−77	74.6	Not determined[d]		

[a] Error limits ± 5%.
[b] At 20°C.
[c] No outer-sphere reaction is observed.
[d] The corresponding reaction mode is too weak to allow the determination of the temperature dependence with enough precision.

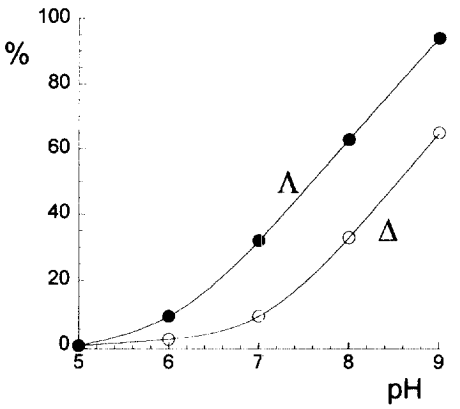


Fig. 2. Amount (%) of electron-transfer mediated fixation of [Co^{III}(promp)] to wt azurin as a function of pH. Open circles: Δ-[Co((R,R)-promp], filled circles: Λ-[Co((*S*,*S*)-promp)]. Reaction conditions: [wt-az] ca. 2×10^{-4} M; [Co(promp)] = $2 \cdot 10^{-3}$ M; buffers; 0.1 M; acetate (pH 5.0); MES (pH 6.0); phosphate (pH 7.0); Tris–Cl (pH 8.0); borate (pH 9.0); $T = 55$°C.

Some characteristic values determined in this way are collected in Table 3. The most striking feature coming from these data is the much higher activation enthalpy and the less negative activation entropy observed for the inner-sphere reaction. This behaviour is apparently not significantly changed with pH.

In some cases rate constants for both enantiomers of the same reagent and for both reaction pathways can be obtained. In these cases it becomes possible to determine the enantioselectivity for the reactions at each site as well as the selectivity between the different sites for each enantiomer. An example is given in Table 4. It is interesting to mention that in this example, the reduction of azurin by [Co(promp)], the selectivity observed is only due to the inner-sphere reaction, whereas in the case of the reaction between plastocyanin and [Co(alamp)], described elsewhere, both, inner- and outer-sphere reactions show strong, but opposite selectivity [32].

Table 4
Stereo- and site selection in the electron transfer between azurin and Δ- or Λ-[Co^{II}(promp)][a]

	k_{global} ($M^{-1}s^{-1}$)	k_{OS}[b] ($M^{-1}s^{-1}$)	k_{IS}[c] ($M^{-1}s^{-1}$)	Site selection = k_{OS}/k_{IS}
Δ-[Co((*R*,*R*)-promp)]	0.50	0.48	0.025	19.2
Λ-[Co((*S*,*S*)-promp)]	0.58	0.49	0.091	5.4
Enantioselection $= k_\Delta/k_\Lambda$	0.86	0.98	0.27	

[a] pH 7.0; $T = 30$°C.
[b] OS = outer-sphere.
[c] IS = inner-sphere.

5. Discussion and outlook

The first question of interest is to know, whether or not the observed selective behaviour can be rationalized in terms of stereochemical and reactivity properties of the different systems involved. In order to answer this question some molecular modelling studies have been carried out [39] and show that His-87 as a reactive site in plastocyanin is accessible for [Co(alamp)] but not for [Co(promp)]; explaining the absence of the inner-sphere reaction due to a higher steric requirement of the latter. Furthermore, it can bee seen that in the energetically most favourable arrangement Λ-[Co((*S*,*S*)-alamp)] can form one, possibly two, hydrogen bonds with the protein, whereas such a stabilisation does not occur in the sterically most favourable arrangement of its enantiomer. On the other hand the uncoordinated His-83 in azurin is easily accessible and the stereoselectivity observed in the inner-sphere reaction with [Co(promp)] is explained by nonbonding stereo effects. In this case too, the sense of stereoselectivity, which is determined by a difference in the activation enthalpy, can be understood, molecular modelling shows the intermediate with the Λ-isomer to be more stable compared to its enantiomer.

An other observation needing some comments is the higher activation enthalpy and the more negative activation entropy of the inner-sphere reactions. This is a surprising result because one would expect a stabilisation of the transition state by the coordination of the imidazole unit to the Co^{II} complex. The coordination equilibria (4) have been studied in detail [40]

$$[Co^{II}(L)] + im \leftrightarrows [Co(L)im] \quad (4)$$

and the corresponding thermodynamic values for [Co^{II}(promp)] are $K^{25} = 130 \pm 7$; $\Delta H = -15.4 \pm 0.6$ kJ mol^{-1} and $\Delta S = -8.6 \pm 1.7$ J K^{-1} mol^{-1}. Assuming that the stability of binding to a free imidazole molecule and to the imidazole unit of his-83 in azurin are not very different, it is concluded that under the prevailing reaction conditions not more than 10% of the deprotonated form of the protein is bound to the Co^{2+} complex in the precursor equilibrium and that the observed activation enthalpy is decreased by about 15 kJ mol^{-1} by the stabilisation of the ground state due to the precursor formation. Deprotonation should not be of a major influence and this is confirmed by the values of $\Delta H^{\#}$ and $\Delta S^{\#}$ at pH 7–9. Whereas the inner-sphere contribution strongly increases in this pH interval, the activation enthalpy is only moderately reduced and remains significantly higher than the corresponding value for the outer-sphere pathway. On the other hand, the activation parameters for the latter remain essentially unchanged in agreement with the proposed pH independent outer-sphere pathway. The large differences in the activation parameters between the inner- and the outer-sphere reactions might therefore be a consequence of either a conformational change of the protein or/and a stronger desolvation, both due to a closer approach of the reagent to the protein surface in the inner-sphere pathway.

In the present communication we have given an overview of the most significant results obtained in our exploratory studies of the use of chiral reagents in electron-transfer reactions involving metalloproteins. We feel that the new technique of the

electron-transfer mediated binding of chiral coordination compounds to a protein surface, can furnish useful information and could enlarge, together with other analytical methods, our knowledge of stereochemical interactions occuring at protein surfaces. The field of possible applications can be considerably extended by: (i) the study of other metalloproteins, including those for which the primary function is not electron transfer, such as superoxide dismutase; (ii) by using other redox active metal centres, like Cr^{2+}, to target different coordinating groups; and (iii) by using the whole pool of known or new, specially designed, chiral ligands.

Acknowledgements

We greatly wish to thank the Swiss National Science Foundation for the uninterrupted financial support of our research in the field of chiral recognition in electron-transfer reactions.

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