Interaction between the Metals in Cobalt(II)–Copper(II), Cobalt(II)–Chromium(III) and Iron(II)–Chromium(III) Cation Pairs in the Presence of α-Amino Acids and Acetate Anion in Aqueous Solutions

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Changes in visible absorption have been found for cobalt(II)–copper(II), cobalt(II)–chromium(III) and iron(II)–chromium(III) cation pairs compared with separate metals in the presence of α-amino acids and acetate anion in aqueous solutions; it is concluded that bimetal cations stabilized by the ligands are formed.

We have observed in some experiments that Co^{II} in its complex with histidine was protected from oxidation by air in the presence of Cu^{II}. We assumed that this observation might indicate an interaction between some transition metals in their complexes with α-amino acids (AA). Because of the important role of some of these metals in biological systems their possible interaction in complexes with AA seemed to be of potential interest. Interaction through metal–metal bonding is known for solid salts of some metals, including Cu^{II} carboxylates[1] and was suggested for some cobalt complexes.[2] We have not found, however, any reports in the literature on interaction between transition metals in aqueous solution. An interaction between two metals might lead to a change in their visible absorption compared with the separate cations, and we have investigated the visible absorption of Co^{II}–Cu^{II}, Co^{II}–Cr^{III}, Fe^{II}–Cr^{III}, and Mn^{II}–Cr^{III} metal pairs in aqueous solution, containing His, Ala, and Ser as AA ligands. The absorption was measured in the presence and absence of acetate anion.

$Co(OAc)_2{\cdot}4H_2O$–$CoCl_2{\cdot}6H_2O$, $CuSO_4$–$Cu(OAc)_2{\cdot}H_2O$, $FeSO_4$, $MnSO_4$, and $CrCl_3{\cdot}6H_2O$ were used for the preparation of the metal solutions to which the solid AA was added (2 equiv. per metal). The ratio of the metals was 1 : 1. Absorption spectra were measured on Beckman Model 35 Spectrophotometer. The behaviour of the Co^{II}–Cu^{II}–His system was also studied by t.l.c. Results are presented in Table 1 and Figures 1—3. In all the cation pairs investigated, except Mn^{II}–Cr^{III}, a distinct effect of metal 1 on the absorption of metal 2 in the presence of AA + OAc was observed, indicating an interaction between the two metals (Table 1). The effect of Co^{II} in the presence of His (His·HCl) is especially informative, because of the complete disappearance of the cobalt–His absorption (Figures 1 and 3). Metal 1 causes a broadening of the metal 2 absorption towards shorter wavelengths and increases its intensity compared with metal 2 + AA + OAc. A shift of the absorption accompanied by about a twofold increase in its intensity occurs for Cu^{II} and Cr^{III} (metal 2) in the presence of AA + OAc compared with AA or OAc only. This suggests a bimetal interaction (Cu–Cu, Cr–Cr) also in these cases.[3,4] His in the absence of OAc causes an interaction between the metals too, but Ala and Ser do not (Table 1). For Co–Cu–His–OAc and Co–Cu–His different absorption curves were obtained indicating formation of two different complexes (Figure 1). An analogy between the absorption curves 2 and 4 in Figure 1 and 3, 1, and 2 in Figure 2 suggests that the role of His is similar to that of Ala(Ser) + OAc in interaction between the metals.

The influence of metal 1 on the metal 2 absorption in the presence of AA + OAc (or His alone) indicates that the ligands† stabilize the common bimetal cation causing an

Table 1. Interaction between metals demonstrated by a change of absorption (and t.l.c. data).

Metal 1	Metal 2	AA	OAc[a]	Interaction[a]
Co^{II}	Cu^{II}	His	Y	Y
		His	N	Y
		Ala, Ser	Y	Y
		Ala, Ser	N	N
Co^{II}	Cr^{III}	His·HCl	Y	Y
		His	N	Y
		Ala, Ser	Y	Y
		Ala, Ser	N	N
Fe^{II}	Cr^{III}	His·HCl, Ser	Y	Y
Mn^{II}	Cr^{III}	His·HCl	Y	Y/N[b]
		Ser	Y	N

[a] Y = presence, N = absence. [b] Y/N, possibility of a weak interaction.

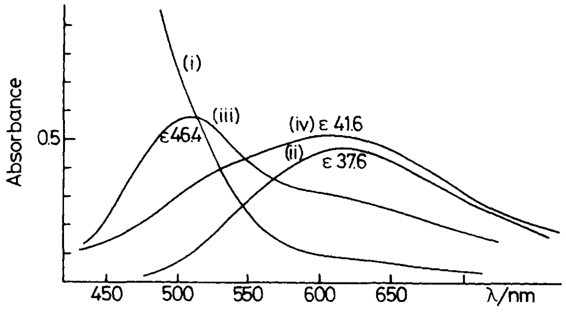

Figure 1. Influence of His and OAc on absorption of Co^{II}, Cu^{II}, and Co^{II} + Cu^{II}. (i) $Co(OAc)_2{\cdot}2His$; (ii) $CuSO_4{\cdot}2His$; (iii) $Co(OAc)_2$–$CuSO_4{\cdot}4His$; (iv) $CoCl_2$–$CuSO_4{\cdot}4His$. Concentrations of metals 2.5×10^{-2} M for all curves.

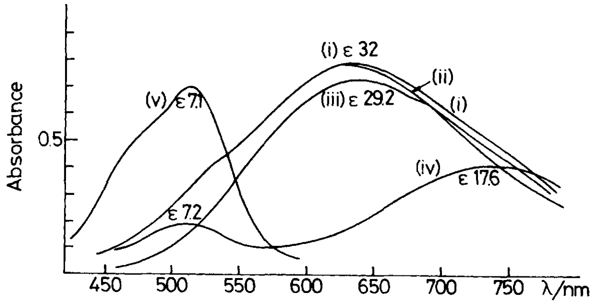

Figure 2. Influence of Ala, Ser, and OAc on absorption of Co^{II} + Cu^{II}. (i) $Co(OAc)_2$–$CuSO_4{\cdot}4Ala$; (ii) $Co(OAc)_2$–$CuSO_4{\cdot}4Ser$; (iii) $Cu(OAc)_2{\cdot}2Ala$; (iv) $CoCl_2$ + $CuSO_4{\cdot}4Ser$ or $Co(OAc)_2$ + $CuSO_4$; (v) $Co(OAc){\cdot}2Ser$, or $Co(OAc)_2$, or $CoCl_2$.

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† In contrast to AA, ethylenediaminetetra-acetic acid (EDTA) does not change absorption of Co^{II} + Cu^{II}; an absorption curve with two maxima due to Co and Cu was obtained in the presence of Na_2 EDTA + OAc.

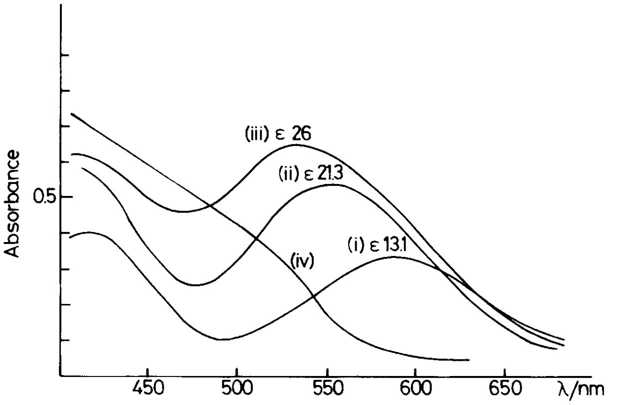

Figure 3. Influence of His·HCl and OAc on the absorption of Co^{II}–Cr^{III} 2 h after preparation of the solutions. (i) $CrCl_3$·His-HCl; (ii) $CrCl_3$·2OAc·2His·HCl; NaOAc used as OAc source; (iii) $Co(OAc)_2$–$CrCl_3$·4His·HCl; (iv) $Co(OAc)_2$·2His·HCl. Concentrations of metals 5×10^{-2} M for all curves. His forms a suspension with Co^{II} + Cr^{III} which disappears slowly. Estimation of the absorption of $Co(OAc)_2$–$CrCl_3$·4His and $CoCl_2$–$CrCl_3$·4His solutions after 24 h gave almost identical curves with $\lambda_{max.}$ 515 nm (ε ~ 65).

interaction between the metals. This suggestion is supported by the t.l.c. behaviour of the Co–Cu–His complex. For Co–His one dark-brown spot was present which apparently corresponded to the Co^{III}–His complex, formed as a result of oxidation by the air of Co^{II} during the developing process. Rapid darkening of the Co^{II}–His solutions in contact with the air was observed in test-tubes. For Co–Cu–His three spots were present, but none of them corresponded either to Co–His or Cu–His, indicating that oxidation of Co^{II} was inhibited by Cu^{II}. This observation is particularly interesting, because it suggests different redox properties of the bimetal cation compared with the interacting metals.

There are two different paths for an interaction between the metals in a polynuclear complex: (i) through metal–metal bonding or (ii) through a ligand bridge. There is no possibility for chelation by AA of two metals separated by a bridging ligand and this is evidence for path (i), where formation of stable six-membered rings between AA and two directly bound metals is possible. Further data are necessary to explain definitively the character of these interactions between complexes of the transition metals and AA + OAc in aqueous solution.

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References

1 A. G. Massey, in 'Comprehensive Inorganic Chemistry,' Pergamon Press, Oxford, 1973, Vol. 3, p. 67.

2 J. W. Mellor, 'A Comprehensive Treatise on Inorganic and Theoretical Chemistry,' Longmans, 1957, Vol. 14, p. 689.

3 Complexes of Cu^{II} with AA have been extensively studied and there are many publications as well as review works on this subject; biological aspects of Cu^{II}–AA are, for instance, widely presented in: 'Trace Elements in the Pathogenesis and Treatment of Inflammation, Agents and Actions Supplements,' Vol. 8 (AAS 8), Birkhäuser Verlag, 1981. Spectroscopic properties of such complexes are discussed in: F. A. Cotton and R. A. Walton, 'Multiple Bonds between Metal Atoms,' Wiley, New York, 1982. We have not found, however, any information in the published data connected with our observations on Cu^{II} behaviour in the presence of AA + OAc.

4 In contrast to Cu^{II} no metal–metal bonding has been described for Cr^{III} in its crystalline salts. It is known, however, for Cr^{II} and is suggested to be stronger than Cu^{II}–Cu^{II} bonding: C. L. Rollinson, in 'Comprehensive Inorganic Chemistry,' Pergamon Press, Oxford, 1973, Vol. 3.

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