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What is the Reason for the *cis* Configuration of Diaquo-Cu^{2+}-(2,2'-Bipyridyl)$_2$ in Aqueous Solution?

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It is well known that the Cu^{2+}-2,2'-bipyridyl 1:2 complex exists in aqueous solution at room temperature as the cis diaquo isomer. So far this geometry has always been attributed to a steric repulsion between the 6,6'-H atoms of the two 2,2'-bipyridyl ligands in a trans *arrangement. Based on the qualities of mixed-ligand Cu^{2+} complexes it is concluded that the* cis *configuration of $Cu(2,2'\text{-bipyridyl})_2^{2+}$ is* cis *due to electronic reasons (back donation) and not to steric hindrance.*

Introduction

In aqueous solution Cu^{2+} usually shows a strong preferance for the formation of square-planar complexes, as can be judged from their stabilities[1-3] and catalytic[4] behavior. For example, the difference in stability between the Cu^{2+}-ethylenediamine 1:1 and 1:2 complexes[1] is much less than the difference between the corresponding 1:2 and 1:3 complexes: log K^{Cu}_{CuL} – log $K^{CuL}_{CuL_2}$ = 10.72–9.31 = 1.41, and log $K^{CuL}_{CuL_2}$ – log $K^{CLu_2}_{CuL_3}$ = 9.31–(–1.0) = 10.3. These data suggest that the third ethylenediamine can bind only monodentatally.[1,2,5]

The corresponding data for the Cu^{2+}-2,2'-bipyridyl complexes are quite different: log K^{Cu}_{CuL} – log $K^{CuL}_{CuL_2}$ = 8.10 – 5.50 = 2.60, and log $K^{CuL}_{CuL_2}$ – log $K^{CLu_2}_{CuL_3}$ = 5.50 – 3.40 = 2.10.[6] The approximate equality of these differences suggests that in aqueous solution at room temperature the Cu^{2+}-2,2'-bipyridyl 1:2 complex exists as the *cis* diaquo isomer. Such an «octahedral» structure is in agreement with spectral observations (anomalously large λ_{max} value)[7-9] and recent ESR[9,10] and NMR[10] studies. In addition, the Cu^{2+}-2,2'-bipyridyl 1:2 complex is the only known fourfold coordinated Cu^{2+} complex with a catalase-like activity.[11,12]

Discussion

So far, the reason for this unexpected geometry of the Cu^{2+}-2,2'-bipyridyl 1:2 complex has always been attributed to a steric repulsion between the 6,6'-H atoms of the two 2,2'-bipyridyl ligands in a *trans* arrangement.[8,13-16] However, if this explanation is correct, it is hard to see why in the Cu^{2+}-N,N'-diethylethylenediamine system an octahedral arrangement is not also preferred. That steric hindrance occurs in this system is obvious from the difference, log K^{Cu}_{CuL}– log $K^{CuL}_{CuL_2}$ = 8.79–5.57 = 3.22,[17] which is much larger than the mentioned corresponding value of the Cu^{2+}-ethylenediamine system. Again, a *cis* configuration in the 1:2 complex would lower the steric hindrance, however, no evidence for this was ever observed.

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[4] Fourfold coordinated Cu^{2+} complexes are inactive in the decomposition of H_2O_2 as the substrate has no possibility to coordinate; H. Sigel, *Angew. Chem.*, *81*, 161 (1969); *Int. Ed.*, *8*, 167 (1969).

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[9] Yu.I. Skurlatov and A.P. Purmal', *Russian J. Phys. Chem.*, *43*, 880 (1969).

[10] M. Noack and G. Gordon, *J. Chem. Phys.*, *48*, 2689 (1968). - Quite recently it has been shown that the glassy ers spectrum of « $Cu(Bipyridyl)_2^{2+}$ » at 77° K is largely a superposition of the esr spectra of the disproportionation products $Cu(Bipyridyl)^{2+}$ and $Cu(Bipyridyl)_3^{2+}$; F.A. Walker and H. Sigel, *Inorg. Chem.*, *11* (1972) in press.

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[12] Additionally, a recent X-ray crystallographic determination of the structure of $[Cu^{2+}\text{-}(2,2'\text{-bipyridyl})_2(ONO)]NO_3$ revaled a *cis* distorted octahedral stereochemistry; I..M Procter and F.S. Stephens, *J. Chem. Soc.* (*A*), 1248 (1969).

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[15] F.P. Dwyer, H.A. Goodwin, and E.C. Gyarfas, *Austral. J. Chem.*, *16*, 544 (1963).

[16] B.J. Hathaway, I.M. Procter, R.C. Slade, and A.A.G. Tomlonson, *J. Chem. Soc.* (*A*), 2219 (1969).

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The high stability of mixed-ligand Cu^{2+} complexes containing 2,2′-bipyridyl has also been attributed to steric hindrance in the Cu^{2+}-2,2′-bipyridyl 1:2 complex.[8,18] It was said that in the mixed-ligand complex the steric repulsion between the two ligands is absent allowing the formation of a planar structure.[19] However, this explanation cannot be correct, since in mixed-ligand Cu^{2+} complexes containing 2,2′-bipyridyl and a second ligand with O atoms as donors, positive values for the difference, $\Delta\log K = \log K^{Cu(bipy)}_{Cu(bipy)L} - \log K^{Cu}_{CuL}$,[20] were observed.[21-23] So it is hard to see why, *e.g.*, the coordination of pyrocatecholate to the hydrated Cu^{2+} ion should be sterically more hindered than the cordination of the same ligand to the Cu^{2+}-2,2′-bipyridyl 1:1 complex ($\Delta\log K = +0.43$); if in this example any steric repulsion occurs, one would expect just the opposite.[23]

Therefore, recently the mentioned high stability of mixed-ligand Cu^{2+} complexes containing 2,2′-bipyridyl was attributed to the ability of 2,2′-bipyridyl to form π bonds by the transition of metal d electrons to vacant π type ligand orbitals.[22-24] We think that the same effect, this means the formation of such π (back donating) bonds, is responsible for the *cis* orientated structure of the diaquo Cu^{2+}-2,2′-bipyridyl 1:2 complex in solution. A *cis* orientated, octahedral configuration allows a stronger and more independent charge transfer between the metal ion and the ligands than a *trans* arrangement.

The *cis* configuration of the Cu^{2+}-*o,o′*-phenanthroline 1:2 complex was also attributed to a steric repulsion between the 2,9-H atoms of the phenanthroline molecule.[8,13-15,18] However, in this case the same argument holds as given for the Cu^{2+}-2,2′-bipyridyl systems. In addition, again pyrocatecholate forms more stable complexes with the Cu^{2+}-*o,o′*-phenanthroline 1:1 complex than with the free, hydrated Cu^{2+} ion ($\Delta\log K = +0.35$).[25]

Note added in proof. Very recently two papers appeared which are of interest for the present discussions. In one of them[26] a strong point is made for « the steric effect in bis(2,2′-bipyridyl) and bis(1,10-phenanthroline) metal compounds », while the other one[27] describes the crystal structure of $Cu(2,2'\text{-bipyridyl})_2(C10_4)_2$. Indeed, the crystal structure determination gives evidence for some steric interference between the 6,6′-H atoms, *i.e.* the pyridyl groups are somewhat twisted toward each other (they « are arranged in a flattened tetrahedral manner »). However, Nakai[27] concludes: « Rougly speaking, the coordination polyhedron around the copper atom is a tetragonally distorted octahedron. The copper atom lies almost on the least-squares plane defined by the nitrogen atoms (average Cu-N = 1.99 Å), and the Cu-O bonds (2.45 and 2.73 Å) are approximately normal to this plane »[28] Hence, the presence of two bipyridyls in the coordination sphere of Cu^{2+} does not on principle preclude a *trans* arrangement. At this point it must be noted that replacement of $C1O_4^-$ by (the stronger ligand) NO_2^- results in a *cis* configuration.[12] Obviously, the second ligand, *i.e.* the coordinating qualities of the anion, has an intrinsic influence on the structure. Therefore, these results support further the above conclusion that the *cis* configuration of $Cu(2,2'\text{-bipyridyl})^{2+}$ in aqueous solution is due to electronic effects. Finally, based on their paper, « steric effects in a distorted square planar bis-(2,2′-bipyridyl) metal complex: X-ray crystal structure of aquobis-(2,2′-bipyridyl)palladium(II) nitrate », Carty and Chieh[29] conclude « ...there is no firm basis for predicting the instability or non-existence of $M(bipy)_2^{n+}$ species, where M is a metal generally adopting square planar stereochemistry, purely from steric considerations ».

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(19) Evidence is given for the planar structure of the mixed 2,2′-bipyridyl-Cu^{2+}-ligand complexes.[8] This conclusion is confirmed by esr studies; F.A. Walker, H. Sigel, and D.B. McCormick, manuscript in preparation. - The dimer, $[Cu(2,2'\text{-bipyridyl})OH]_2$, in acqueous solution is also considered to be planar.[9] A recent X-ray study of $[Cu(2,2'\text{-bipyridyl})OH]_2SO_4 \cdot 5\ H_2O$ showed a dimeric unit in which each Cu atom is bonded to five donor atoms in a distorted square-pyramidal configuration, the two basal planes being slightly angular to each other. The more distant apical atoms are an oxygen atom of sulfate in the one case and of a water molecule in the other; A.T. Casey, B.F. Hoskins, and F.D. Whillans, *Chem. Commun.*, 904 (1970); *cf.* also R.J. Majeste and E.A. Meyers, *J. Phys. Chem.*, *74*, 3497 (1970).

(20) $K^{Cu(bipy)}_{Cu(bipy)L} = [Cu(bipy)L]/([Cu(bjpy)][L])$; $K^{Cu}_{CuL} = [CuL]/([Cu][L])$.

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(24) P.R. Huber, R. Griesser, and H. Sigel, *Inorg. Chem.*, *10*, 945 (1971).

(25) H. Sigel, P.R. Huber, R. Griesser, and B. Prijs, results to be published.

(26) E.D. McKenzie, *Coord. Chem. Rev.*, *6*, 187 (1971).

(27) H. Nakai, *Bull. Chem. Soc. Japan*, *44*, 2412 (1971).

(28) This is confirmed by the esr data of $Cu(bipyridyl)_2(ClO_4)_2$; these are typical for axially-symmetric complexes in which the coordination geometry is at least approximately square-planar, and the unpaired electron is in the $d_{x^2-y^2}$ orbital of copper. F.A. Walker, H. Sigel, and D.B. McCormick, submitted for publication.

(29) A.J. Carty and P.C. Chieh, *Chem. Commun.*, 158 (1972).