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Low Frequency Infrared Modes of Copper(II) Polyamine Complexes and Related Kinetic Factors of Ligand Dissociation

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The proton-assisted ligand dissociations of polyamines from Cu(II) and Ni(II) complexes have been generally attributed to the protonation of a pendant donor of the chelate ring which has fully ruptured [1]. Back-reaction is therefore prevented by protonation of the lone pair of the pendant group. An alternate possibility of the direct attack of H_3O^+ on the M^{n+}–N bond pair was proposed early in the development of the studies in these mechanisms [2], but the concept was largely discounted on electrostatic grounds due to the repulsion of the M^{n+} cation for the proton. Siddiqui and Shepherd recently showed that the dissociation of $Cu(tren)(H_2O)^{2+}$ exhibits both pathways which can be identified by their differing sensitivity to the presence of counterions [3]. The direct attack path utilizes an ion pair, $[H_3O^+, X^-]$, to intercept a partially ruptured Cu^{2+}–NH_2R bond prior to the time for the rupturing chelate ring to rotate out of the first coordination sphere of Cu(II) [3]. The activation parameters for the direct attack path of $Cu(tren)H_2O)^{2+}$ closely matches those for dissociation of the chain polyamines en; dien, trien, dach and [9]aneN_3 from Cu(II) [3]. Therefore it appears that the direct attack path is actually the one utilized in most dissociations of Cu(II) polyamines. Read and Margerum have found a similar acid-assisted dissociation of en from $Ni(en)(H_2O)_4{}^{2+}$ but the incoming proton was anchored in a *cis* position to the Ni^{2+}–NH_2R bond by coordination of a neutral HX molecule, such as CH_3COOH, at a labile H_2O site prior to Ni–N bond rupture [1d].

A kinetic order for the value of k_1, the initial step in the dissociation of polyamines from Cu(II), was found to be tren (direct attack) > dien > trien > en > [9]aneN_3 ≫ tren (pendant protonation) [3]. We were interested to know if this order showed a correlation with the Cu–N stretching vibrations or ring deformation modes of this series of Cu(II) polyamine chelates, or if other factors such as solvation or geometrial distortion of the ground state complex were to play an obvious rate determining role in the ligand dissociation reactions of these species.

These questions prompted us to examine the infrared spectra of Cu(II) polyamines in the low frequency region. We have also studied the solution geometries of these complexes by the ESR technique [4]. The results of the ESR spectra are given in a separate manuscript; the Cu(II) polyamines of this study all exhibit rhombically distorted square-planar strcutures [4]. A similar IR/ESR study of Cu(II) polyamines, augmented by quantum mechanical calculations, has been elegantly advanced by Tsipis *et al.* [5]. Similar Cu(II) polyamine salts, such as $PF_6{}^-$, $NO_3{}^-$ or $ClO_4{}^-$, to those reported in our measurements were used in the Tsipis study [5]. The IR assignments agree where en or trien complexes were examined. Several additional polyamine arrangements (tren, dien, and tn) are reported here that have not been studied in detail by other workers.

Experimental

Cu(II) Salts

$[Cu(en)_2](NO_3)_2$, $[Cu(en)_2](PF_6)_2$, $[Cu(tn)_2](NO_3)_2$, $[Cu(tn)]_2(PF_6)_2$, $[Cu(trien)](PF_6)_2$, $[Cu(dien)(H_2O)](NO_3)_2$, $[Cu(tren)(H_2O)](NO_3)_2$ and $[Cu(tren)(H_2O)](PF_6)_2$ were prepared by evaporation of a $Cu(NO_3)_2$ or $Cu(PF_6)_2$ solution of the appropriate polyamine. Ligands for $[Cu(tet\ a)(H_2O)](ClO_4)_2$ and $[Cu(tet\ b)(H_2O)](ClO_4)_2$ were prepared by the methods of Hay *et al.* [6].

IR Spectra

Crystals were collected and pressed into KBr and polyethylene pellets to record IR spectra. Spectra in the 600 to 250 cm^{-1} region were recorded with a Perkin-Elmer Model 599 infrared spectrophotometer (in Valparaíso, Chile). Assignments and confirmation of certain assignments are based on the available literature [5].

Results and Discussion

$Cu(en)^{2+}$ has been examined previously [5, 7–9] as well as many other en complexes of Pt(II), Pd(II), and Co(III) [10–13]. The low energy IR spectrum of $Co(trien)^{3+}$ [5, 13] and $Co(tren)^{3+}$ [14, 15]

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have also been reported. These literature reports have assisted our assignments for the various polyamines. The salts containing PF_6^- as the counterion also exhibit a ν(PF) ~ *ca.* 550 cm^{-1} [16, 17]. The PF_6^- counterion exhibits semi-coordination to the Cu(II) center in some of the polyamine salts, but the Cu–N frequencies are little changed whether PF_6^- or NO_3^- is the counterion.

The main problem is the assignment of the bands corresponding to Cu–N stretching and it is evident that there is still considerable confusion in the literature about the position of this band in ethylenediamine complexes. For instance, Omura *et al.* [8] assigned this fundamental to bands at 472 and 412 cm^{-1} in $[Cu(en)_2](SCN)_2$, supporting the assignment with a normal coordinate analysis. For this same complex, Lever and Mantovani [7] have assigned bands at 412 and 309 cm^{-1} as Cu–N stretch bands. Cyvin *et al.* [18] have reported that the Cu–N stretching modes in $[Cu(NH_3)_4]^{2+}$ occur at 420, 375 and 426 cm^{-1}. This mode would lie at a lower energy in Cu(II) polyamines complexes since the effective mass of the nitrogen atom has been increased. In our series of Cu(II) polyamine complexes we have assigned to Cu–N the bands at *ca.* 401 (en), 404 (tn), 376 (trien), 358 (tren) and 386 (dien) cm^{-1}.

Strong bands at *ca.* 522 (en), 518 (dien), 497 (tn), 526 (trien) and 530 (tren) cm^{-1} have been ascribed to ring deformation. The lower value for $Cu(tn)_2^{2+}$ complexes could be a consequence of the six-membered ring in opposition to the five-membered ring in en and dien. A similar trend can be observed for this normal mode in $[Cu(acac)_2]$ (six-membered ring) and $[Cu(ox)_2]^{2-}$ (five-membered ring), which was assigned to 373 [19] and 420 [20] cm^{-1}, respectively. The high value observed in $[Cu(tren)H_2O]^{2+}$ complexes could be due to the spatial position of the NCCN skeleton. Furthermore, a deformation of NCCN results in the simultaneous deformation of N–Cu–N. There should be coupling between the Cu–N stretch and the NCCN deformation. The correlation observed in the shifts of the bands assigned to ring deformations and those attributed to the Cu–N stretch confirms the present assignment.

The weak bands at 445 (en), 439 (tn) and 423 (tren, trien) cm^{-1} could be assigned to another Cu–N mode or to ring deformation. However the band observed at *ca.* 451 cm^{-1} for the complex $[Cu(dien)H_2O](PF_6)_2$ is too strong to be considered as due to Cu–N stretching, as well as those recorded at *ca.* 355 cm^{-1} in the $Cu(tn)_2^{2+}$ complexes. Therefore these are assigned as ring deformations.

Ethylenediamine itself absorbs at *ca.* 468 cm^{-1} as a consequence of an NH_2 rocking vibration [21]. We have assigned this fundamental to the band observed at *ca.* 470 ± 6 cm^{-1} in all the complexes of our study.

TABLE I. Observed IR Bands of tet a, tet b, $[Cu(tet\ a)H_2O](ClO_4)_2$ and $[Cu(tet\ b)H_2O](ClO_4)_2$ (cm^{-1}) in KBr Pellet

tet a	Cu(tet a)-blue	tet b	Cu(tet b)-red
500sh	500	530sh	530sh
490	480	500	490
460	460	483	478
438sh	412	450	455
375	385vw	412	415
335	335	365	363
285	300	325	330
		315	320
		290	

The bands at *ca.* 336 cm^{-1} for $[Cu(tren)H_2O]^{2+}$ and $[Cu(dien)H_2O]^{2+}$ could be assigned to Cu–O stretching. Nakagawa and Shimanouchi [22] have assigned this normal mode to a band at 440 cm^{-1} for $[Cu(H_2O)_4]^{2+}$. There should be an expected shift of this vibration to lower energy, because of the weakness of the Cu–O bond as a result of the amine chelation with the Cu(II) polyamines.

The macrocyclic complexes $[Cu(tet\ a)(H_2O)](ClO_4)_2$ and $[Cu(tet\ b)(H_2O)](ClO_4)_2$ (red and blue isomers) are known to have CuN_4O donor sets that are $\sim C_{4v}$ [23, 24] for tet a; $\sim C_{4v}$ (red) and D_{3h} (blue) for tet b [25]. It would be useful to compare these complexes with the linear or branched polyamine series. The IR data collected for the free ligands and $[Cu(tet\ a)(H_2O)](ClO_4)_2$ (blue) and $[Cu(tet\ b)(H_2O)](ClO_4)_2$ (red) are given in Table I. These would give closed-ring donor sets similar to $[Cu(trien)](PF_6)_2$.

The ligands tet a and tet b present many relatively weak bands in the low region energy (600–300 cm^{-1}), which are due to NH_2 rocking, CH_2 rocking, macrocycle breathing and macrocycle deformation out of plane. The spectra of the Cu^{2+} complexes also offer many bands at similar positions to those presented by the ligands. The pattern of the four IR spectra look almost the same. Therefore it was not possible to assign a band to the Cu–N stretching with assurance. The frequency of this normal mode may be below 300 cm^{-1}. The Cu(II) phthalocyanine complex has the Cu–N vibration assigned at 236 cm^{-1} [26]. If this is the case, the Cu–N stretch is outside the limit of Perkin-Elmer 599 IR in this study.

The values of ν(Cu–N) follow the order en (404) > dien (386) > trien (376) > tren (358 cm^{-1}). This is *not* the kinetic order of k_1: tren (496) > dien (348) > trien (295) > en (126) ≫ tren (pendant path) (3.0 s^{-1}) [3]. There is a modest correlation with the ring deformation order with the kinetic k_1 order: tren (538) > trien (526) > dien (518) > en (515 cm^{-1}), however the range of ring deformation frequencies vary by only 4.3% while the rates change by 394%. The failure of the Cu–N stretch to follow the same order of these systems to form CuL* is not all that surprising. The ν(Cu–N) measures the stretching of the Cu(II) polyamine as a 'neutral' Cu^{2+}–NH_2R bond unit rather than a 3-center Cu-HN^{3+} system. The kinetic distortion to form CuL* involves participation of the H_3O^+ or H_3O^+, X^- ion pair to assist bond weakening of the activated complex where $\Delta H^{\ddagger}$, is found to be tren (5.71) < trien (9.66) < dien (10.6) en (13.3 kcal/mol) in ClO_4^- medium [3]. In the absence of a strong correlation between barriers or rates with the Cu–N stretch or ring deformation modes, one probably concludes that the solvation or presence of the ion pair H_3O^+, X^- in the vicinity of the distorting bond plays an important role in establishing the kinetic order. Evidence from the presence or absence of N-shf coupling in the spectra of Cu(II) complexes with polyamine and imidazole donors shows that the exchange rate of the N donors is remarkably influenced near a pH value of 7 by the presence of the proton or a general acid donor even in dmso: water glasses at 113 K [4]. Such factors are eliminated in the solid state with PF_6^- and NO_3^- salts, where ν(Cu–N) is a measure of bond strength (related to force constant) in the absence of the solvation and ion pair influence required for the 3-centered intermediate in ligand dissociation. The presence of en last in the order tren > dien > trien > en also suggests that a more strongly H-bonded chelate fragment of CuL^{2+} or CuL_2^{2+} with its solvent cage might work against ligand dissociation by making the Cu–N bond more ionic with a greater negative charge on the N donor and a poorer leaving group. Although this arrangement might also favor attraction of H_3O^+, X^- in the bond pair region, it would surely increase the dissociation energy of the unit, raising the kinetic barrier in solution. This should be displayed more by Cu-$(en)_2^{2+}$ than the more hydrophobic chain polyamines; and indeed its barrier is higher by *ca.* 3 kcal/mol [3].

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