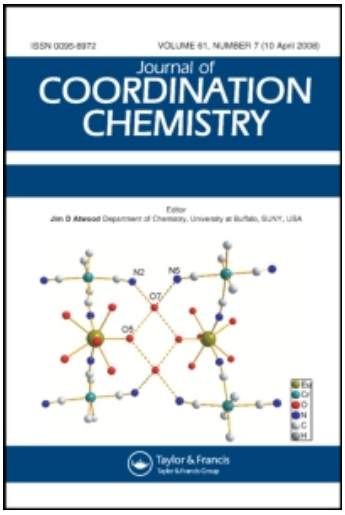

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Ion Association and Proton Exchange Studies of Mixed Ligand Co(III) Complexes of *N,N*-Bis(Carboxymethyl)Glycine as Studied by Nuclear Magnetic Resonance Spectroscopy

Chinmay Chatterjee[a]; Alka Phulambrikar[a]; Subroto Das[a]
[a] Department of Chemistry, Indian Institute of Technology, Bombay, India

To cite this Article Chatterjee, Chinmay , Phulambrikar, Alka and Das, Subroto(1990) 'Ion Association and Proton Exchange Studies of Mixed Ligand Co(III) Complexes of *N,N*-Bis(Carboxymethyl)Glycine as Studied by Nuclear Magnetic Resonance Spectroscopy', Journal of Coordination Chemistry, 21: 3, 231 — 236
To link to this Article: DOI: 10.1080/00958979009409720
URL: http://dx.doi.org/10.1080/00958979009409720

J. Coord. Chem. 1990, Vol. 21, pp. 231–236
Reprints available directly from the publisher
Photocopying permitted by license only

ION ASSOCIATION AND PROTON EXCHANGE STUDIES OF MIXED LIGAND Co(III) COMPLEXES OF *N,N*-BIS(CARBOXYMETHYL)GLYCINE AS STUDIED BY NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

CHINMAY CHATTERJEE*, ALKA PHULAMBRIKAR and SUBROTO DAS

Department of Chemistry, Indian Institute of Technology, Powai, Bombay 400 076, India.

(Received July 29, 1989, in final form January 9, 1990)

Monodiamine (1,2-diaminoethane, 1,2-diaminopropane or 1,3-diaminopropane) and dinitro Co(III) complexes with *N,N*-bis(carboxymethyl)glycine (H_3nta) have been prepared and characterized by electronic, IR and ^{1}H NMR spectroscopy. The association of amine protons with chloride ions and pyridine-d_5 and their relative exchange rates *in situ* have been studied by ^{1}H NMR spectroscopy. The stereoselective approach of the anion at the amine centre is found to dominate ion association and proton exchange processes. Present experimental results offer information as regards the three dimensional structure of the complexes in solution.

Keywords: *N,N*-bis(carboxymethyl)glycine, diamines, cobalt(III) complex, proton exchange, ion association

INTRODUCTION

Ion association can occur when an anion binds with an ionizable proton on a coordinated ligand *via* hydrogen bonding. The importance of the structure of ion associated species lies in the fact that kinetic forms and steric courses of several reactions of metal complexes in non-aqueous solvents are governed by ion association.[1] The conventional means of obtaining ion association constants from conductometric or spectrophotometric measurements do not offer information regarding the directional nature of ion association. However, ^{1}H NMR methods prove to be very useful as information about both the magnitude and directional nature of ion association can be obtained and the method has attracted some attention in recent years. Ion association and proton exchange studies for the *cis*-$[Co(en)_2X_2]^+$ system using ^{1}H NMR[2,3,4] reveals that ion association is stereoselective and occurs *via* hydrogen bonding. In order to gain more insight concerning the origin of stereoselectivity in ion association and proton exchange of coordinated amine hydrogens, the studies have been extended to aminopolycarboxylatodiamine complexes as the presence of the quadridentate ligand might induce more selectivity in the mode of association. This paper reports direct and convenient synthetic procedures for nta Co(III) complexes of which the 1,3-diaminopropane and the dinitro complexes have been prepared for the first time. The detailed assignment of the ^{1}H NMR spectra has been achieved. Ion association and proton exchange studies have been carried out and these confirm the ^{1}H NMR assignments.

* Author for correspondence.

EXPERIMENTAL

The ligand *N,N*-bis(carboxymethyl)glycine (H_3nta) was obtained from the Aldrich Chemical Co., Inc., and was used without further purification.

[Co(nta)(en)]·H_2O

a) Direct oxidation: A mixture of $CoCO_3$ (0.012 mol. 1.45 g) and H_3nta (0.01 mol. 1.91 g) in water (40 cm^3) was stirred at 60°C until CO_2 evolution ceased. To it, 1,2-diaminoethane (en) (0.01 mol. 0.60 g) and activated charcoal (0.3 g) was added and the mixture oxidized by bubbling air through it for 12 h at room temperature. After removing the charcoal, the filtrate was concentrated to about 10 cm^3 and allowed to stand at room temperature. The resulting violet crystals were recrystallized from the minimum amount of hot water, washed successively with water and ethanol, and finally air dried. Yield, 70%.

b) Substitution: *Trans*-$[Co(en)_2Cl_2]$ Cl (0.005 mol, 1.43 g) and H_3nta (0.005 mol. 0.96 g) were dissolved in water (50 cm^3). After raising the pH of the solution to 6–7 by addition of sodium hydroxide, the mixture was heated on a steam bath until crystals started to appear. Upon cooling to room temperature the crude product containing violet and yellow crystals separated. The more soluble yellow material was separated from the violet crystals by repeated washing with cold water. Evaporation of the initial washings to a small volume yielded yellow crystals which were identified as $[Co(en)_3]Cl_3$ on the basis of reported spectral data.[5] The violet crystals of $[Co(nta)(en)].H_2O$ were recrystallized as in procedure (a). Yield, 60%. Found: C, 29.30; H, 4.82; N, 12.60%. $C_8H_{14}Co\ N_3O_6H_2O$ requires C, 29.54; H, 4.92; N, 12.92%. The 1,2-diaminopropane (pn) complex was prepared by both methods whereas the 1,3-diaminopropane (pd) complex was obtained only by the direct oxidation procedure. [Co(nta)(pn)].0.5 H_2O, found: C, 32.50; H, 5.20; N, 12.60%. $C_9H_{16}CoN_3O_6.0.5H_2O$ requires C, 32.72; H, 5.25; N, 12.72%. [Co(nta)(pd)].H_2O, found: C, 31.20; H, 5.25; N, 12.20%. $C_9H_{16}CoN_3O_6.H_2O$ requires C, 31.85; H, 5.31; N, 12.39%.

$Na_2[Co(nta)(NO_2)_2]$

$Na_3[Co(NO_2)_6]$ (0.005 mol, 2 g) and anhydrous sodium carbonate (0.005 mol, 0.53 g) were added to water (5 cm^3) and the reaction mixture was stirred until the solution changed from brownish yellow to red, resulting in the formation of $Na_3[Co(NO_2)_4CO_3]$. To it, after cooling in ice, H_3nta (0.005 mol, 0.96 g) was added in small portions with constant stirring to give a red coloured oily substance. The mother liquor was decanted off and ethanol (50 cm^3, in portions) added until a red solid separated. The solid was filtered, washed with an ice cold ethanol–water (2:1) mixture then absolute ethanol, and finally air dried. Yield, 75%. Found: C, 18.50; H, 1.50; N, 10.72%. $C_6H_6CoNa_2N_3O_{10}$ requires C, 18.70; H, 1.56; N, 10.91%. *Trans*-$[Co(N\text{–}N)_2Cl_2]^+$ (N–N = en, pn) and $Na_3[Co(NO_2)_6]$ were prepared according to reported procedures.[6,7]

Electronic spectra were recorded with a Shimadzu UV-260 spectrophotometer and IR spectra with a Perkin-Elmer 681 spectrophotometer. ^{1}H NMR spectra were run on Varian XL-100 and Bruker 500 MHz FT-NMR spectrometers. C,H,N analyses were obtained with a Carlo-Erba automatic microanalyser.

Results and discussion

Akamatsu *et al.*[8] earlier reported the preparation of [Co(nta)(N–N)] (N–N = en, pn)

as involving the substitution of labile groups in *cis*-$[Co(en)(NH_3)_2Cl_2]^+$ by nta. This method suffers from an inherent disadvantage, however, as the preparation of the precursor complex, *cis*-$[Co(N–N)(NH_3)_2Cl_2]^+$ involves a multistep synthesis. In contrast, a rapid direct synthetic route has been developed. This involves the reaction between *trans*-$[Co(N–N)_2Cl_2]^+$ with H_3nta at pH 6. Despite the kinetic inertness exhibited by the coordinated diamine towards substitution, the reaction is found to be facile under mild conditions, a manifestation of the multidentate effect with respect to the aminopolycarboxylate ion.

The electronic spectra of the series of complexes examined here (Table I) exhibit two low energy broad bands corresponding to $^1A_{1g} \longrightarrow {}^1T_{1g}$ and $^1A_{1g} \longrightarrow {}^1T_{2g}$ transitions, respectively. The positions of the bands are similar to those observed for analogous *mer*-$Co^{III}N_3O_3$ systems.[8]

TABLE I
Electronic and ^{1}H NMR data for the complexes.

	Electronic data*				^{1}H NMR Chemical shifts[a]		
	Band I		Band II		>N–CH_2–COO^-	>N–CH_2–COO^-	$-NH_2$
Complex	λ_{max}	ε	λ_{max}	ε	(R ring)	(G ring)	
[Co(nta)(en)]·H_2O	522	1540	366	1780	4.13, 4.10 3.88, 3.85 (J_{ab} = 15 Hz)	3.83	6.48 4.62[b]
[Co(nta)(pd)]·H_2O	531	1680	369	2080	4.39, 4.36 3.80, 3.77 (J_{ab} = 15 Hz)	3.83	5.72 4.26[b]
[Co(nta)(pn)-]·0.5H_2O	524	1670	366	1890	4.54, 4.36 4.34, 4.18 (J_{ab} = 18 Hz)	4.30	[c]
Na_2[Co(nta)$(NO_2)_2$]	515	1980	339	52670	4.22, 4.06 3.76, 3.60 (J_{ab} = 16 Hz)	3.70	[d]

*λ_{max} : Wavelength in nm; ε : Molar extinction coefficient in aqueous solution ($dm^2\ mol^{-1}$). [a] Chemical shifts in ppm relative to TMS. [b] Spectrum recorded in DMSO-d_6 at 500 MHz. [c] Spectrum recorded in D_2O at 100 MHZ. [d] Spectrum recorded in DMSO-d_6 at 100 MHz.

All complexes showed strong IR absorption in the region 1648–1658 cm^{-1}. Characteristic of coordinated carboxyl groups. The diamine complexes exhibited a doublet between 3100–3300 cm^{-1} for the primary amine group. The peaks between 3400–3600 cm^{-1} indicate the presence of water of crystallization. The nitro complex exhibited characteristic nitro group frequencies at 1400–1425 cm^{-1}, 1330–1335 cm^{-1} and 825–840 cm^{-1}, respectively.[9]

In the ^{1}H NMR spectrum of the ligand (nta) in DMSO-d_6, a sharp singlet at 3.50 ppm is observed due to the acetate protons. The 500 MHz NMR spectra of [Co(nta)(pd)]·H_2O in DMSO-d_6 showed that the amine protons of 1,3-diaminopropane appear as two broad resonances at 5.72 and 4.26 ppm, respectively, each with intensity corresponding to two protons. The large difference in chemical shift of the two amines is rationalised on the basis of the different electron donating abilities of ligating groups *trans* to them. Extending Freeman's argument,[10] the resonance at

4.26 ppm is assigned to amine protons on N(1), *trans* to the carboxylate oxygen atom O(1), whereas the amine protons on N(2), *trans* to the tertiary nitrogen atom of nta, N(3), appear at 5.72 ppm. The acetate protons of the ligand undergo splitting on complexation. The AB pattern with centres at 4.38 and 3.78 ppm ($J \sim 15$ Hz) is assigned to the non-equivalently coupled acetate protons of the two chelate rings, (R ring) of nta, which are not coplanar with the diamine ring. The non-equivalence can be accounted for in terms of the magnetic anisotropy of the C–N bond. The sharp singlet at 3.83 ppm is assigned to protons on the acetate ring (G ring), coplanar with the diamine ring. An interesting feature of the methylene resonances of 1,3-diaminopropane is their splitting into three peaks. This is seen but very rarely. They resonate at 2.57, 1.90 and 1.77 ppm with equal (two proton) intensity. This feature indicates the magnetic nonequivalence of the α-CH_2 protons. Extending Freeman's rule, the signal at 2.57 ppm can be assigned to the α-CH_2 protons adjacent to the nitrogen atom *trans* to the tertiary nitrogen N(3). The peak at 1.90 ppm is thus assigned to the α-methylene protons adjacent to nitrogen *trans* to carboxylate oxygen O(1) and the peak at 1.77 ppm to β-CH_2 protons. Similar splitting of methylene resonances is observed in case of the *cis*-$[Co(pd)_2(CN)_2]^+$ complex.[11] ^{1}H NMR data for the other complexes is tabulated in Table I.

The ^{1}H NMR of $[Co(nta)(pn)]\cdot 0.5H_2O$ in D_2O revealed two methyl doublets at 1.50 and 1.27 ppm, indicating the presence of a mixture of isomers.[8] The methyl doublet at 1.50 ppm can be assigned to the *trans*-N_t,N* isomer while the doublet at 1.27 ppm is assigned to the *cis*-N_t–N* isomer (where N_t is the tertiary nitrogen on nta and N* is the nitrogen adjacent to the asymmetric carbons of pn (based on Freeman's argument).[10]

The X-ray crystal structure analysis of $[Co(nta)(pd)]\cdot H_2O$,[12] shows that the two nitrogen atoms of pd, the nitrogen atom and three carboxyl oxygen atoms of nta give a distorted octahedral coordination around the cobalt atom. The six-membered ring formed by the pd ligand adopts a chair conformation.

The coordinated amine protons are found to be most susceptible to ion association. This causes a downfield shift of the signals in the ^{1}H NMR spectrum. In case of the *cis*-$[Co(en)_2X_2]^+$ system, the chemical shift of one particular amine hydrogen was found to be the most susceptible to changes in the nature of counter anions and the concentration of the complex species; this proton was identified as *trans*-H_A. The chemical shift of *trans*-H_B, *cis*-H_A and *cis*-H_B amine hydrogens are, however, not susceptible to the nature of the counter anion to any large extent. Ion association studies during the present investigation were carried out by adding varying volumes of LiCl solution in DMSO-d_6 ([Cl] = 2.4 M), to the complex in DMSO-d_6 and recording the spectrum after each addition. The variation in chemical shifts of amine hydrogens were noted (see Tables IIa and IIb). These results clearly indicate that it is the upfield amine resonance which experiences a downfield shift with increasing concentration of chloride ions in $[Co(nta)(pd)]\cdot H_2O$ and $[Co(nta)(en)]\cdot H_2O$. The downfield shift is indicative of outer sphere association between amine hydrogens and Cl^- ions. An examination of molecular models shows that these amine hydrogens are oriented in such a way that the Cl^- ions experience least localised negative charge while approaching these amines. The amine protons on N(2) exhibit a slight upfield shift with increasing concentration of Cl^- ions. On the basis of their higher acidities, the N(2) amine hydrogens might be expected to associate most. This is not found to be so, as the Cl^- ions "feel" the localized negative charge of the carboxylates while approaching these protons. The association constant (*ca* 2.0) for $[Co(nta)(pd)]\cdot H_2O$ was calculated according to the reported method.[3] The chemical

shift of the downfield portion of the AB quartet (assigned to the H_A proton on the out of plane acetate ring) undergoes a downfield shift with increasing concentration of Cl^- ions. Similar behaviour of the chemical shift of one of the CH_2 protons adjacent to the pyridine ring in the (1,11-bis(2'-pyridyl)-2.6.10-triazaundecane)-Co(III) cation is observed.[13]

TABLE II
Variation of amine chemical shifts (δ in ppm) with increasing concentration of LiCl.

a) $[Co(nta)(pd)]\cdot H_2O$.

Concentration of LiCl (mol dm^{-3})	δ N(2)–H	δ N(1)–H
0.00	5.72	4.26
0.30	5.65	4.58
0.43	5.65	4.70
0.62	5.65	4.80
0.77	5.65	4.82
1.00	5.65	4.85

b) $[Co(nta)(en)]\cdot H_2O$.

Concentration of LiCl (mol dm^{-3})	δ N(2)-H	δ N(1)-H
0.0	6.48	4.62
0.16	6.44	4.72
0.36	6.42	4.79
0.69	6.41	4.85

In view of high donor power of pyridine and the acidity of coordinated amine hydrogens, hydrogen bonding between them is likely. In order to substantiate the electrostatic influence in ion association, the variation of amine chemical shifts in py-d_5/DMSO-d_6 solvents has been studied (Table III). As the pyridine content in the solvent increases, both the amine signals experience downfield shifts, the largest effect being associated with N(2). Since pyridine is a neutral molecule, association will now be governed only by the acidity of the proton. The higher the acidity, the higher will be the extent of association. This confirms that the association by anionic and neutral donors occurs *via* hydrogen bonding and the stereoselective association of anions is governed by electrostatic considerations.

TABLE III
Amine chemical shifts (δ in ppm) in mixed py-d_5/DMSO-d_6 solvents.

	$[Co(nta)(pd)]\cdot H_2O$		$[Co(nta)(en)]\cdot H_2O$	
% py-d_5 (v / v)	δ N(2)–H	δ N(1)–H	δ N(2)–H	δ N(1)–H
0	5.72	4.26	6.47	4.62
17	5.97	4.48	6.71	4.84
30	6.12	4.60	6.78	4.89
48	6.32	4.77	7.06	5.14

The coordinated amines undergo rapid exchange in D_2O. Proton exchange involves attack of OD^- at the amine centre, thereby resulting in decrease in amine proton intensity in the ^1H NMR spectrum. For *cis*-$[Co(en)_2X_2]^+$ complexes,[4] when $X = NO_2$, the amine hydrogen which ion-associates most is also the one which is exchanging most rapidly. However, when X = acac, OX or CN, the amine proton ion associating most is not the one which is exchanging fastest. As no proton exchange data are available for mixed ligand aminopolycarboxylate (diamino)-Co(III) complexes, the present study was undertaken. Proton exchange studies were carried out by adding D_2O (0.03–0.06 cm^3) to the complex in DMSO-d_6 and measuring the changing areas under the amine protons as a function of time. Analysis of the experimental results indicates that in both $[Co(nta)(pd)]\cdot H_2O$ and $[Co(nta)(en)]\cdot H_2O$ complexes the upfield amine hydrogens are exchanging at least five times faster than the downfield amine hydrogens. The former are also the protons which ion-associate most. This is consistent with the idea that the first stage of proton transfer involves specific N–H– –OD^- bond formation.[14] Hence proton exchange is also found to be dominated by the ease of approach of OD^- at the amine centre rather than the acidity of amine hydrogens.

ACKNOWLEDGEMENTS

The use of the 500 MHz FT-NMR national facility at TIFR, Bombay, is gratefully acknowledged.

REFERENCES

1. D.W. Watts, *Pure Appl. Chem.*, **51**, 1713 (1979).
2. H. Nakazawa, U. Sakaguchi and H. Yoneda, *Bull. Chem. Soc. Jpn.*, **53**, 1595 (1980).
3. H. Nakazawa, U. Sakaguchi and H. Yoneda, *J. Am. Chem. Soc.*, **104**, 3885 (1982).
4. H. Nakazawa, U. Sakaguchi and H. Yoneda, *Inorg. Chem.*, **20**, 973 (1981).
5. D.A. Johnson and A.G. Sharpe, *J. Chem. Soc.*, A, 7986 (1966).
6. M. Krishnamurthy, *J. Inorg. Nucl. Chem.*, **34**, 3953 (1972).
7. W.G. Palmer, "Experimental Inorganic Chemistry," (Cambridge University Press, Cambridge, 1965), pp. 529–533.
8. K. Akamatsu, T. Komarita, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **54**, 3000 (1981).
9. K. Nakamoto, "Infrared Spectra of Inorganic Coordination Compounds," (Wiley Interscience, New York, 1970).
10. W.A. Freeman, *J. Coord. Chem.*, **7**, 197 (1979).
11. H. Kawaguchi and S. Kawaguchi, *Bull. Chem. Soc. Jpn.*, **46**, 3453 (1973).
12. K. Swaminathan, U.C. Sinha, C. Chatterjee, A. Phulambrikar, V.M. Padmanabhan and R. Bohra, *Acta Cryst.*, **C45**, 566 (1989).
13. E. Ahmed, C. Chatterjee, C.J. Cooksey, M.L. Tobe, G. Williams and M. Humanes, *J. Chem. Soc., Dalton Trans.*, 645 (1989).
14. M.L. Tobe, "Inorganic and Bioinorganic Reaction mechanisms," Ed. A.G. Sykes, Vol. 2, (Academic Press, London, 1983), pp. 36–42.