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Synthesis of Some New Polysiloxane Ligand Systems (Iminodiacetate) Part I

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The polysiloxane-immobilized glycinate and iminodiacetate chelating ligand systems of the general formula Ⓟ-$(CH_2)_3N(CH_2CO_2H)_2$ (where Ⓟ represents the polysiloxane network), have been prepared by the reaction of 3-halopropyltrimethoxysilane before or after its hydrolytic polycondensation with tetraethoxysilane and diethyliminodiacetate $HN(CH_2CO_2Et)_2$. The elemental analyses indicate that the replacement of iodine by diethyliminodiacetate ligand groups takes place much easier than chlorine. The iminodiacetate polysiloxane ligand systems show high potential for copper(II) uptake and form 1 : 1 complexes with copper(II).

INTRODUCTION

Various organic functional groups have been attached to silica[1–10] by the reaction of the most widely used coupling agent of general formula R_3SiR', R = OMe or OEt, R′ is an organic functional ligand group. In these systems the alkoxy groups react with hydroxyl groups on the silica surface. More recently porous polyorganosiloxane systems are prepared by hydrolytic sol-gel methods using the tetraethoxysilane $(EtO)_4Si$ as a cross linking backbone agent and the appropriate silane coupling agent R_3SiR'.[11–16] Such siloxane polymer materials can, in principle at least, contain a much higher density of ligand groups than can be achieved by surface silyation, and the ligand groups are securely incorporated is an integral part of siloxane polymer[17]. Variety of organic ligand groups especially those bearing metal-binding groups have been obtained[17, 18–21]. These polysiloxane-immobilized ligand systems have been made because of the lack of selectivity and thermal stability of conventional ion-exchange resins[22] and pollution control[23]. Moreover, they have many potential applications, such as preconcentration and separation of metal ions from aqueous solutions[5, 17, 19] and supports for hydrogenation catalyst[18] and chromatographic stationary phase to separate metal ions[20, 24]. The structural properties have been recently investigated using modern spectroscopic methods[25–32]. In this work a new chelating ligand is incorporated into the polysiloxane matrix; this ligand is iminodiacetate. Different synthetic methods and conditions were used in order to establish the optimum conditions under which maximum density of ligand groups are introduced.

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EXPERIMENTAL

The Microanalytical Service Laboratories in the Department of Chemistry (UMIST), England were used to carry out the elemental analysis of carbon, hydrogen, chlorine, iodine, nitrogen and copper. Results are given in Tables 1, 3–5.

TABLE-1
ANALYTICAL DATA OF PREPARED SILANE-COUPLING AGENTS AND DIETHYLIMINODIACETATE

Compound	% Analysis					C/X	C/N
	C	H	N	I	Cl		
3-Iodopropyl-trimethoxy silane	26.3 (24.8)	5.5 (5.2)	—	41.8 (43.7)	1.0 (0.0)	6.1 (6.0)	—
Diethylamino-diacetatepropyl-trimethoxysilane	36.6 (35.1)	6.5 (6.3)	4.1 (2.9)	6.2 (26.5)	—	—	10.4 (14.1)
Diethylimino diacetate	51.1 (50.8)	8.2 (7.9)	7.3 (7.4)	—	—	—	8.2 (8.0)

Calculated elemental percentages are given in parenthese.

TABLE-2
^{1}H and ^{13}C NMR DATA FOR DIETHYLIMINODIACETATE SYSTEMS

Diethyliminodiacetate $HN(CH_2C(O)OCH_2CH_3)_2$	$—CH_2\underline{CH_3}$	$N—\underline{CH_2}$	$O—\underline{CH_2}$	$H—\underline{N}$	$\underline{C(O)}—O$	$CDCl_3$
^{1}H (ppm)	1.10 (t)	3.29 (s)	4.00 (q)	1.99 (s)	—	7.26
^{13}C (ppm)	14.13	50.08	60.72	—	171.7	77.0

t = triplet, s = singlet and q = quartet

TABLE-3
ELEMENTAL ANALYSIS OF HALOPOLYSILOXANE

Compound	% Analysis				C/X	I/Cl	Time (h)
	C	H	Cl	I			
PC1	11.7 (14.4)	3.2 (2.4)	13.3 (14.3)	—	2.6 (3.0)	—	—
PI1	11.7 (10.0)	2.7 (2.7)	6.5 (5.6)	21.7 (20.3)	2.7 (2.6)	0.82 (0.93)	88
PI2	9.3 (10.6)	2.5 (1.8)	—	30.5 (37)	3.2 (3.0)	—	—

PC1 = Ⓟ—$(CH_2)_3Cl$

PI1 = Ⓟ—$(CH_2)_3I$, made by the reaction of PCl with NaI

PI2 = Ⓟ—$(CH_2)_3I$, made by the reaction of 3-iodopropyltrimethoxysilane with tetraethoxysilane

TABLE-4
ELEMENTAL ANALYSIS OF DIETHYLIMINODIACETATE AND IMINODIACETATE POLYSILOXANES

Ligand	% Analysis C	H	N	I	Cl	C/N
PIDA1	16.7 (30.2)	3.7 (5.3)	1.3 (3.3)	—	11.8 (0.0)	15.0 (10.7)
PIDA2	21.4 (23.6)	4.3 (4.8)	2.0 (1.9)	1.5 (1.4)	6.9 (6.4)	12.5 (14.5)
PIDA3	24.8 (27.5)	5.0 (5.0)	2.7 (2.8)	1.5 (1.3)	—	10.7 (14.5)
PIDA3h	18.1 (18.2)	3.8 (2.6)	2.9 (3.0)	—	6.3 (0.0)	7.4 (7.0)
PIDA4	21.6 (32.8)	4.0 (4.9)	2.4 (3.5)	6.8 (0.0)	1.3 (0.0)	10.5 (11.0)
PIDA4h	13.2 (15.9)	2.4 (2.3)	2.3 (2.6)	—	2.7 (0.0)	6.8 (7.0)

PIDAl = Ⓟ-$(CH_2)_3N(CH_2CO_2Et)_2$
PIDAh = Ⓟ-$(CH_2)_3N(CH_2CO_2H)_2$

TABLE-5
ANALYTICAL DATA FOR COPPER(II) COMPLEXES OF IMINODIACETATE POLYSILOXANE

Complex	% Analysis C	H	N	Cu	N/Cu
PIDA2h Cu(II) complex	17.9	3.7	1.7	5.0	1.5
PIDA3h Cu(II) complex	16.1	3.6	2.3	7.7	1.4
PIDA4h Cu(II) complex	12.4	3.6	1.9	5.6	1.6

Infrared spectra in the range of 4000–200 cm^{-1} were obtained on a Perkin-Elmer 598 infrared spectrophotometer using KBr disks.

NMR spectra were measured on Bruker 300 and 200 MHz NMR spectrometers.

Reagents of R_4Si, R_3SiR', ($R = OEt$, OMe; $R' = (CH_2)_3Cl$) were purchased from Aldrich Chemical and used without further purfication. The iminodiacetic acid was also obtained from Aldrich Company and used without further purification.

All solvents were dried before use. Diethylether was stored over sodium wire. Ethanol and methanol were dried and stored over molecular sieves. Acetone was dried by standing three days over anhydrous potassium carbonate and filtered. The filtered solvent was then dried over 4A molecular sieves, and then the solvent was distilled before use. Toluene was dried over sodium wire and distilled before use.

Preparation of 3-iodopropyltrimethoxysilane: This was prepared as previously described[20] as follows: To a solution of sodium iodide (38.4 g, 0.25 mol) in dry acetone (250 cm^3), 3-chloropropyltrimethoxysilane (48.9 g, 0.245 mol) was added dropwise at room temperature. The reaction mixture was heated under reflux for 48 h at 70°C. The solvent was removed and the residue was extracted repeatedly with diethylether (4 × 100 cm^3), to give a light yellow oil material. The elemental analyses are given in Table-1.

Preparation of diethyliminodiacetatepropyltrimethoxysilane: A round-bottom flask was charged with 3-iodopropyltrimethoxysilane (4.2 g, 0.014 mol) and diethyliminodiacetate (5.5 g, 0.029 mol). The mixture was refluxed at 90°C for 40 h. Yellow oily material was obtained. The oily material was used without further purification. Analyses are shown in Table-1.

Preparation of diethyliminodiacetate: Iminodiacetic acid (30.0 g, 0.4 mol) was stirred with 300 cm^3 of absolute ethanol to which thionyl chloride (93.86 g, 0.8 mol) was added dropwise. The reaction mixture was stirred and refluxed at 80°C until all the iminodiacetic acid was dissolved. The reaction was allowed to proceed under reflux for further 5 h. The mixture was cooled to room temperature and the excess of ethanol and SO_2 was removed by evaporation under vacuum. The residue was dissolved in 100 cm^3 distilled water and 150 cm^3 of chloroform was added. Then 33% of sodium hydroxide solution was added dropwise with shaking after each addition, so that the diethyliminodiacetate passed into the chloroform and the pH of the solution was adjusted to around 7. The aqueous layer was extracted repeatedly with chloroform (4 × 150 cm^3). The layer of chloroform was separated and then dried for 2 h over anhydrous $MgSO_4$. The chloroform was removed at reduced pressure and the residue product was dried *in vacuo* (0.1 torr) for at least 1 h. See Table-2 for ^1H and ^{13}C NMR analysis and Table-1 for elemental analysis.

Preparation of 3-chloropropylpolysiloxane (PCl): This was prepared as previously described[20–25] as follows: Tetraethoxysilane (52 g, 0.25 mol) was added to stirred solution of 3-chloropropyltrimethoxysilane (24.82 g, 0.125 mol) in 50 cm^3 dry methanol. 15.75 cm^3 of 0.42 M HCl was added as catalyst. The mixture was stirred for 6 h at room temperature, then left to gel for two days. The polymer was dried in an oven at 100°C overnight. The polymer was ground and washed with distilled water until clear washings were obtained. The material was then washed with methanol and diethyl ether. The solid product was dried in vacuum (0.1 torr) at 80°C for at least 2 h and stored *in vacuo* in a desiccator at room temperature. The results are presented in Table-3.

Replacement of chlorine with iodine on 3-chloropropylpolysiloxane (P-I1): This was prepared as previously described[20] as follow: The 3-chloropropylpolysiloxane (20 g) was added to sodium iodide (80 g, 0.5 mol) in 880 mL of dry acetone. The mixture was stirred and refluxed at 70°C for 72 h. The product was filtered, washed with water, methanol and diethyl ether and then dried *in vacuo* (0.1 torr) in 80°C for 3 h.The elemental analyses are given in Table-3.

Preparation of 3-iodopropylpolysiloxane (P-I2): This was prepared as previously described[13] as follow: 3-Iodopropyltrimethoxysilane (44.52 g, 0.15 mol) was added to stirred methanolic solution of tetraethoxysilane (62.52 g, 0.3 mol) and aqueous hydrochloric acid (5.75 mL, 0.42 M). The mixture was stirred for 6 h at room temperature, then left to gel for 3 days. The solid product was dried at 100°C overnight. The polymer was ground and washed with distilled water, methanol, and diethyl ether. The product was dried *in vacuo* (0.1 torr) at 80°C. The analytical data are shown in Table-3.

Preparation of diethyliminodiacetaepolysiloxane (PIDA1, PIDA2, PIDA3): These polysiloxane ligand systems were made by two methods: First by the reaction of either chloro- or iodopolysiloxane with diethyliminodiacetate as follows: Diethyliminodiacetate (5.29 g, 0.028 mol) was added to iodopolysiloxane (PI1 or PI2) or chloropolysiloxane (PC1). The mixture was stirred and refluxed at 95°C for different times ranging from 6–72 h. The reaction products PIDA1, PIDA2 and PIDA3 respectively were filtered off, washed with 0.001 M NaOH, distilled water, methanol, and diethyl ether. The products were dried *in vacuo* (0.1 torr) and stored in a vacuum desiccator over phosphorus(V) oxide. The analytical analyses are given in Table-4.

The other method was the polycondensation of diethyliminodiacetopropyltrimethoxysilane with tetraethoxysilane as follows: Diethyliminodiacetopropyltrimethoxysilane (3.51 g, 0.01 mol) was added to stirred solution of tetraethoxysilane (4.16 g, 0.02 mol) in 10 cm^3 of methanol and 1.98 cm^3 of 0.42 M HCl as a catalyst. The mixture was stirred for 4 h where gelation occurred. The solid product (PIDA4) was crushed and dried at 100°C overnight. The polymer was washed with distilled water, methanol and diethyl ether, then dried *in vacuo* (0.1 torr) for 2 h at 80°C. The analytical data are shown in Table-4.

Hydrolysis of ethylglycinate and diethyliminodiacetate functionalised polysiloxanes (PIDA3h, PIDA4h): A known amount of the required functionalised polysiloxane (5.0 g) was stirred and refluxed with 50 cm^3 hydrochloric acid (5 M) at 100°C for 24 h. The mixture was cooled to room temperature, filtered and the product was washed with water, methanol and diethyl ether. The material was then dried *in vacuo* (0.1 torr) at room temperature for 3 h. The elemental analyses are given in Table-4.

Metal uptake: The appropriate polysiloxane iminodiacetate ligands (0.1 g) were shaken with twice the required amount of an aqueous solution of copper(II) ion (0.1 M). After 24 h contact time at room temperature the polysiloxane-metal complex was separated from the solution by filtration, washed with distilled water, dry methanol and diethyl ether. The resultant blue solid products were dried *in vacuo* (0.1 torr) for at least 2 h at 100°C and kept in vacuum desiccator at room temperature. The elemental analyses for the copper(II) complexes are given in Table-5.

RESULTS AND DISCUSSION

Synthesis: Polysiloxane-immobilized iminodiacetate ligand system was made by hydrolytic condensation of $Si(OEt)_4$ and silane agent $(MeO)_3Si(CH_2)_3N(CH_2CO_2Et)_2$. The hydrochloric acid was used as acid catalyst and gelation occurred after several hours to yield a porous material. An alternative method was used by refluxing the halopolysiloxane with diethyliminodiacetate.

Preparation of starting materials: In this work 3-iodopropyltrimethoxysilane was obtained as previously described[20] by the reaction of 3-chloropropyltrimethoxysilane with excess of NaI as shown in equation (1). The elemental analyses are given in Table-1. From the analysis it is obvious that most of chlorides have been replaced by iodides.

$$(CH_3O)_3Si(CH_2)Cl + NaI \xrightarrow[70°C]{\text{acetone}} (CH_3O)_3Si(CH_2)_3I + NaCl \qquad (1)$$

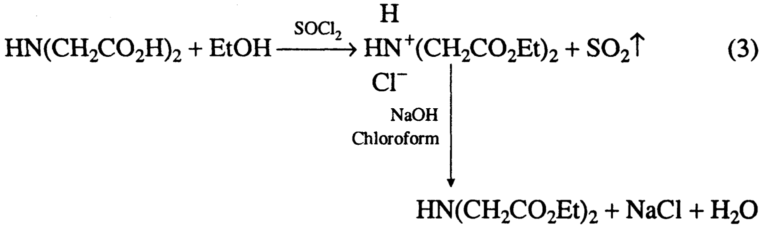
The diethyliminodiacetatepropyltrimethoxysilane coupling agent was made by the reaction of 3-iodopropyltrimethoxysilane with diethyliminodiacetate as described in equation (2).

$$(MeO)_3SiCH_2CH_2CH_2I + HL \longrightarrow (MeO)_3SiCH_2CH_2CH_2L + HI \qquad (2)$$

$L = N(CH_2CO_2Et)_2$

The elemental analyses for this silane coupling agent are given in Table-1. The results show higher nitrogen percentage compared with the expected one, which reflects the lower C/N found ratio (10.4) compared with the expected value (13.8). This may be attributed to some generated hydrogen iodide that may escape from reaction mixture during the reflux into the solution.

The diethyliminodiacetate was prepared by the reaction of iminodiacetic acid in absolute ethanol in the presence of thionyl chloride as given in equation (3).



$$HN(CH_2CO_2H)_2 + EtOH \xrightarrow{SOCl_2} \overset{H}{\underset{Cl^-}{HN^+}}(CH_2CO_2Et)_2 + SO_2\uparrow \qquad (3)$$

$$\xrightarrow[\text{Chloroform}]{\text{NaOH}} HN(CH_2CO_2Et)_2 + NaCl + H_2O$$

The elemental analysis of the product is shown in Table-1. The resulting product was also characterized by ^{1}H NMR, ^{13}C NMR, and FTIR spectra, The ^{1}H NMR and ^{13}C NMR chemical shifts assignments are given in Table-2.

Preparation of polysiloxane-immobilized ligand systems: The chloropolysiloxane system was made as previously described[20, 25] by hydrolytic polycondensation of $(MeO)_3Si(CH_2)_3Cl$ and $(EtO)_4Si$, to give a porous material (PCl). The elemental analyses for the chloropolysiloxane are given in Table-3. The iodopolysiloxane system can be prepared either by the reaction between chloropolysiloxane with sodium iodide (PI1) or by obtaining the 3-iodopropyltrimethoxysilane first, then inserting the new product into the sol-gel mixture (PI2) which allowed replacement of iodine by organic metal-binding ligand groups. The elemental analyses for these materials are given in Table-3.

In the case of chloropolysiloxane PCl where 2 : 1 molar ratio of tetraethoxysilane and 3-chloropropyltrimethoxysilane was used, the lower carbon and chloride percentages than the expected ones could be explained due to the formation of soluble oligomers that dissolved during the washing process. This is probably due to different rate of hydrolysis of the alkoxysilane, which lead to self-condensation and forming small non-cross-linked soluble oligomers.

In the reaction between chloropolysiloxane with sodium iodide (PI1), it is found that after 88 h not all the chlorides were replaced by iodide (Table-3, and Fig. 1). Fig. 1 shows the analytical data versus the time of the reaction. The results indicate that replacement of chlorine by iodine was not complete and only half of the chlorine was reacted, which may suggest that some of the chlorides are imbedded deep into the matrix and hence not available for replacement by iodine after 88 h.

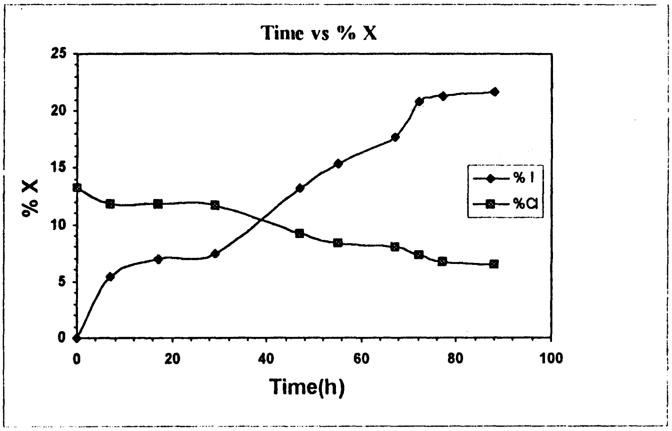


Fig. 1 Analytical data versus time, replacement of chloride with iodide for the chloropolysiloxane PC1.

The iodopropylpolysiloxane can also be prepared by producing the 3-iodopropyltrimethoxysilane, which can then react with tetraethoxysilane in the presence of hydrochloric acid as catalyst forming a porous material of iodopropylpolysiloxane PI2. The analyses are given in Table-3. The results show lower cabon and iodine percentages than the expected values. This may be explained due to small soluble oligomers formed by self-condensation. This was evident from the found C/I molar ratio (Table-3).

The polysiloxane-immobilized iminodiacetate ligand system was made by two methods, first by the reaction of halopolysiloxane with diethyliminodiacetate as shown in equation (4).

$$ⓟ\text{—}(CH_2)_3X + HN(CH_2CO_2Et)_2 \xrightarrow{-HX} ⓟ\text{—}(CH_2)_3N(CH_2CO_2Et)_2 \quad (4)$$

X = Cl or I.

The analyses for the polysiloxane-immobilized iminodiacetate ligand systems are given in Table-4. The decreasing of halogen percentage and the increase in the percentage of carbon after the replacement of halogen by iminodiacetate group is evident from the introduction of iminodiacetate groups into the surface of polysiloxanes.

In comparison with the reactivity of the three halopolysiloxanes, chloropolysiloxane (PC1) and two iodopolysiloxanes (PI1) and (PI2), towards the reaction with diethyliminodiacetate, it is found that in the case of the chloropolysiloxane most of the chlorides are not replaced (PIDA1) whereas, for the other two iodopolysiloxanes PI1 and PI2 the iodides have been mostly replaced (PIDA2 and PIDA3). This is because the iodine is a much easier leaving group than Cl (Table-4).

The second method was used to introduce the ligand group diethyliminodiacetate before polymerisation by the reaction of diethyliminodiacetate with 3-iodopropyltrimethoxysilane then the resulting product was hydrolyzed and polycondensed with tetraethoxysilane in 1:2 molar ratio respectively to give the required polysiloxane-immobilized ligand system PIDA4. From elemental analysis data (Table-4) the results indicate that the possible reason for the lower carbon and nitrogen percentages than the expected values are due to the formation of lower molecular weight groups that dissolved during the washing process.

The polysiloxane-immobilized diethyliminodiacetate ligand systems PIDA3 and PIDA4 were hydrolyzed by HCl. The elemental analyses are given in Table-4. The results show that the C/N molar ratios are decreased from 10.7 and 10.5 for PIDA3 and PIDA4 to 7.4 and 6.8 respectively. This suggests that most of the ethoxy groups were transformed to the acid form, which was confirmed by infrared spectra (Figure 2c).

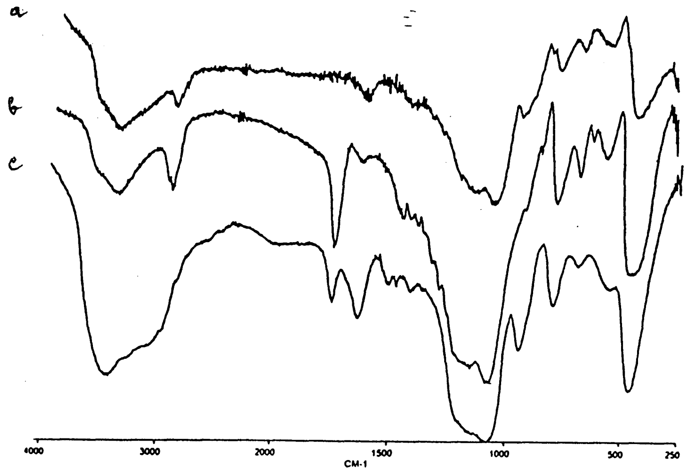
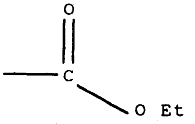
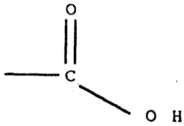


Fig. 2. FTIR spectra for the polysiloxane-immobilized systems:
(a) Iodopolysiloxane system (PI2).
(b) Diethyliminodiacetate polysiloxane system (PIDA)
(c) Iminodiacetate polysiloxane system (PIDAh).

Infrared spectra

The FTIR spectra for the polysiloxane-immobilized ligands show three characteristic regions at 3300 cm^{-1}, 1740 cm^{-1} and 1100 cm^{-1} corresponding to ν(OH) or ν(NH), ν(C═O) and ν(Si—O) vibrations respectively. These assignments are based on IR data obtained from literature[33]. The IR spectra for iodopolysiloxane and diethyliminodiacetate polysiloxane and its acid hydrolysis product are shown in Fig. 2. The appearance of an absorption of 1745 cm^{-1} for the diethyliminodiacetate polysiloxane (Fig. 2a) due to the ester ν(C=O) stretching vibration is strong evidence for the introduction of the diethyliminodiacetate group into the polymer surface. In the hydrolyzed product, two absorption bands at 1740 and 1630 cm^{-1} are found (Fig. 2c) which are probably attributed to stretching vibration of ester and acid forms ν(C=O) and bending vibration δ(OH) respectively as follows:





The presence of low intensity absorption band at 1740 cm^{-1} may confirm that not all ester ethoxy groups (—OEt) have transformed to the acid form (—OH).

Metal uptake

The microanalytical data for the interaction of polysiloxane iminodiacetate ligands with un-buffered (pH = 4.5) solutions of copper(II) chloride, are listed in Table-5. This ligand undergoes some further loss of carbon and nitrogen, presumably by leaching of oligomeric material. It might be expected that the maximum metal-loading achievable would correspond to one metal ion per one iminodiacetate ligand group.

In the case of PIDA2h and PIDA4h, the composition approximates 1.5 of iminodiacetate per one metal ion; this might indicate that some 2:1 or 1:1 complexes are formed. On one hand the formation of 1:1 complexes would probably be favoured on thermodynamic grounds because the resulting complex is stable due to formation of a five-membered ring, where iminodiacetate with symmetric side chains forms 1:1 complexes with metal ions if they are suitably placed. On the other hand, the formation of 1:1 complexes was observed for PIDA3h (N/Cu molar ratio = 1.4) which means that more of 1:1 complexes were formed than 2:1.

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