



SYNTHESIS AND CHARACTERIZATION OF N-(I-MORPHOLINOBENZYL) SEMICARBAZIDE MANGANESE (II) AND IRON (II) COMPLEXES

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ABSTRACT

The interaction of ethanolic solution of semicarbazide hydrochloride, benzyldehyde and morpholine yielded N-(I-Morpholinobenzyl) Semicarbazide Schiff base. The Schiff base complexes of manganese(II) and iron(II) were synthesized by refluxing the mixture of ethanolic solutions of the Schiff base and metal(II) chlorides, respectively. These complexes were characterized by gravimetry, spectrophotometry, potentiometry, molar conductance and infrared analyses. The Schiff base and the complex compounds are not soluble in water, slightly soluble in most common organic solvents but are readily soluble in methanol and ethanol. The molar conductance of the manganese(II) and iron(II) Schiff base complexes measured are 3.78 and 6.90 $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$, respectively, indicating their non-electrolytic nature. The potentiometric studies revealed a pKa of 5.40 for the Schiff base. The standard Gibb's free energy of Mn(II) and Fe(II) Schiff base complexes determined are -65.79KJmol^{-1} and -60.35KJmol^{-1} , respectively. The ratio of metal ion to Schiff base determined potentiometrically and spectrophotometrically for the complex compounds is 1: 2. The IR spectrum of the Schiff base shows bands observable in the two Schiff base complex compounds, indicating the coordination of the Schiff base to the copper ion.

Key Words: Schiff base, azomethine, benzyldehyde, potentiometry, spectrophotometry, semicarbazide hydrochloride, morpholine.

INTRODUCTION

The condensation of primary amine with either an aldehyde or a ketone yields Schiff base (Holm *et al.*, 1966; Hobday and Smith, 1972; Pierre, 1987). The carbonyl group of the aldehyde gives aldimines while that of ketone gives ketoimines. It has been known that different metal ions on interaction with Schiff bases yield chelates, for example; Tsumaki (1983) reported [Co(sal₂-en) Complex which received a great attention owing to its ability to undergo reversible adduct formation with molecular oxygen. The oxygenation ability of the complex was first recognized by Hassan *et al* (1998), however, the mechanism for the oxygenation process was not well understood until recently with the advent of modern physical techniques. Xishi *et al* (2003) reported the synthesis and characterization of a novel Schiff base ligand formed from the condensation of 2, 2-bis (P-methoxyphenylamine) and Salicylaldehyde and its Mn(II), Co(II) and Cu(II) complexes. The Ben Saber *et al* (2005) reported the synthesis and characterization of Cr(III), Fe(III), Co(II) and Ni(II) complexes with a Schiff base derived from 4-dimethylamino benzaldehyde and primary amines. The chemical analysis data showed the formation of (1:1) metal - ligand ration and a square planar geometry was suggested for Co(II) and Ni(II) complex while an octahedral structure for Cr(III) and Fe(III) complexes. In another report, Cu(II), Co(II), Ni(II) and Zn(II) complexes of new heterocyclic Schiff base derived from 1-amino - 5- benzoyl - 4- phenyl - 1H - pyrimidine - 2- on with salicylaldehyde have been synthesized and

investigated by elemental analysis (Sonmez and Sekerel, 2002). An octahedral geometry was suggested for all the complexes. Ben Saber *et al* (2005), reported the synthesis of a Schiff base derived from salicylaldehyde, and Histidine and its complex compounds with divalent transition metal ions. The complexes were investigated by elemental analysis and were found to be of 1:1 metal to ligand ratio.

Transition metal Schiff base complexes are used in various fields, such as medicine, agriculture, industries etc. For example, [Co(acac₂-en)] in dimethylformamide, pyridine and substituted pyridines proved to be involved in oxygen metabolism (Hanna and Mona, 2001). Transition metal complexes with 1, 10 - phenanthroline and 2, 2 - bipyridine are heavily used in petroleum refining (John *et al.*, 1976). Schiff base formed by the condensation of 1-formyl-2-hydroxy-3- naphtholic arylamide with O-hydroxyl or O-methoxy aniline complexes of Co (II), Ni (II), Cu (II) and Zn (II) are useful as figments (Gupta *et al.*, 2002). Oxovanadium Complexes have been found strongly active, against some type of Leukemia (Dong *et al.*, 2002). Transition metal complexes derived from a number of amino acids have been reported to have biological activity (Zahid *et al.*, 2007). Morad *et al.*, (2007), reported the antibacterial activity of Ni(II) with salicylaldehyde and 2-amino-benzoic acid complex. Popova and Berova (1981) reported that copper is good for liver function, its level in blood and urine has influence in pregnancy disorders, nephritis hepatitis, leprosy, anemia and Leukemia in children.

This paper reports the synthesis and characterization of manganese (II) and iron (II) N-(1-

morpholinobenzyl)semicarbazide complexes, as exhaustive literature search revealed rare information.

MATERIALS AND METHODS

In preparation of reagents, chemicals of analytical grade purity were used. All weighings were observed on electrical metler balance model AB 54. melting point, decomposition temperature were determined on Gallenkamp melting point apparatus. IR spectra measurements were recorded using Fourier Transformed IR Genesis series model in Nujol in the region 40000 – 400cm. electrical conductivity measurements were carried out using conductivity meter model 4010. UV-visible spectral measurements were done on a Pye Unicam UV-visible spectrophotometer.

Synthesis of Mannich Base:- N-(1-Morpholinobenzyl) Semicarbazide.

To 20cm³ semicarbazide hydrochloride (11%) solution in ethanol, a 10cm³ of benzaldehyde was added dropwise with constant stirring and then neutralized with ammonia solution. To this solution 10cm³ of morpholine was also added dropwise, while maintaining the stirring for 20minutes. On standing precipitate was observed to form and was separated and recrystallised from hot ethanol as described by Raman *et al.* 2004).

Synthesis of the Metal Complexes

A mixture of 5mmol metal (II) chlorides in ethanol and N-(1-morpholinobenzyl)semicarbazide schiff base (1.25g, 5mmol) solution in ethanol/chloroform mixture (1.6) was refluxed for 3 hours. The resulting mixture was concentrated to about third of its volume and then cooled to 0°C, for 12 hours. The precipitate that formed was filtered, washed with ethanol and dried in vacuo (Raman *et al.*, 2004).

Determination of Dissociation Constant of N-(1-Morpholinobenzyl)semicarbazide

To a 400 cm³ beaker were added 90 cm³ of distilled water, 100cm³ 0.2M KNO₃, 10cm³ of 0.4M N-(1-morpholinobenzyl)semicarbazide and a magnetic stirring bar before the electrodes of a standardized meter were introduced. A 10cm³ of standardized aqueous NaOH was added dropwise with stirring. After each 0.5cm³ addition, the amount of NaOH solution and the corresponding pH were recorded. Points in the 20 to 80 percent titration range were used to calculate the pKa (Gregory *et al.*, 1978).

Determination of Stability Constants of N-(1-Morpholinobenzyl) Semicarbazide Manganese(II) and Iron(II) Complexes

Into a 400cm³ beaker 100cm³ of 0.2M KNO₃, 1mmole of metal (II) chloride, 0.1M HNO₃ and 90cm³ of distilled water were added, respectively. A magnetic stirring bar and sodium salt of the Schiff base, prepared by neutralizing a known quantity of the N-(1-morpholinobenzyl)semicarbazide Schiff base with calculated amount of standardized NaOH solution. After each 0.2cm³ aliquot addition, the corresponding

pH of the stirred reaction mixture was recorded. From the results obtained, stability constant of the complex compound and the number of the coordinated ligands per metal ion were determined (Gregory *et al.*, 1978).

Determination Schiff Base to Metal ion By Continuous Variation Method

The ligands to metal ratio in the complex compounds were determined using "Job's methods" in which one millimolar solutions of the Schiff base and a metal (II) chloride were prepared. By mixing these solutions, mixtures having a total volume of 10cm³ in which the mole fraction of N-(1-morpholinobenzyl)semicarbazide, X, is 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, and 0.9 were prepared. The absorbance of each of these solutions was recorded at a specific wavelength (λ_{max}) at which the metal(II) ion solution absorbs maximally. A plot of absorbance against the ligand's mole fractions was made, from which mole fraction (X) at maximum absorbance was recorded for the mixture containing stoichiometric amount of M²⁺ and ligand from which the number of coordinated Schiff base per a metal ion, n was calculated (Angelici, 1977).

RESULTS AND DISCUSSION

The interaction between morpholine, benzaldehyde and semicarbazide hydrochloride formed N-(1-morpholinobenzyl)semicarbazide Schiff base, a white crystalline product with melting point of 200°C. The metal Schiff base manganese(II) and iron(II) complexes synthesized were crystalline white and yellow, with yield of 65.75% and 61.22% and have decomposition temperatures of 206°C and 210°C, respectively (Table 1). The N-(1-morpholinobenzyl)semicarbazide Schiff base and the metal complexes were not soluble in water, slightly soluble in most common organic solvents but are readily soluble in methanol and ethanol (Table 2). The molar conductance measurement carried out on manganese(II) and iron(II) Schiff base complexes are quite low, indicating their non-electrolytic nature (Table 3). The IR spectra of the free N-(1-morpholinobenzyl)semicarbazide Schiff base shows bands in the region 1565 - 1600cm⁻¹, which are assigned to $\nu(C=N)$ stretching vibration, a fundamental feature of azomethine group, a confirmation of formation of a Schiff base. Bands within this region are also observable in manganese(II) and iron(II) Schiff base complex compounds, an indication that N-(1-Morpholinobenzyl)semicarbazide Schiff base has coordinated to the metal ions.

The broad band at 3440 – 3560cm⁻¹ is assigned to $\nu(O-H)$ stretching vibrational modes in the free Schiff base, which got deprotonated on coordination. However, sharp and broad bands in the range 3345-3580cm⁻¹ have been observed in the complex compounds which are attributed to water of hydration in the complexes.

The bands within 630-740 and 420-480 cm^{-1} were attributed to $\nu(\text{M-O})$ and $\nu(\text{M-N})$ stretching vibrations, respectively, reaffirming the coordination of the Schiff base to the metal ions (Table 4). The elemental analysis of N-(1-morpholinobenzyl)semicarbazide manganese(II) and iron(II) complexes, suggested the molecular formulae, $[\text{MnL}_2] \cdot 4\text{H}_2\text{O}$, and $[\text{FeL}_2] \cdot 2\text{H}_2\text{O}$, respectively. The dissociation constant, pK_a , of N-(morpholinobenzyl)semicarbazide Schiff base (Table 7) determined is 5.40, indicating a weak acid. The stability constant values determined (Table 8) for Mn(II) and Fe(II) Schiff base complexes were 1.24×10^{10} and 8.21×10^{10} , which correspond to the standard Gibb's energies of $-65.79 \text{kJ mol}^{-1}$ and

60.35kJ mol^{-1} , respectively. These low standard Gibb's free energies of the complex compounds explain their good stability, as buttressed by their high decomposition temperatures. The potentiometric analytical results revealed 1:2 metal to N-(1-morpholinobenzyl)semicarbazide Schiff base in both the complex compounds (Tables 9 and 10). This ratio is supported by the results obtained from continuous variation studies on manganese(II) and iron(II) N-(1-morpholinobenzyl)semicarbazide complex compounds (Tables 5 and 6). The elemental analysis of N-(1-morpholinobenzyl)semicarbazide manganese(II) and iron(II) complexes, suggested the molecular formulae, $[\text{MnL}_2] \cdot 4\text{H}_2\text{O}$, and $[\text{FeL}_2] \cdot 2\text{H}_2\text{O}$, respectively.

From the results obtained on the analysis of the two divalent metal N-(1-morpholinobenzyl)semicarbazide complex compounds, the molecular structure in fig 1 below, is proposed.

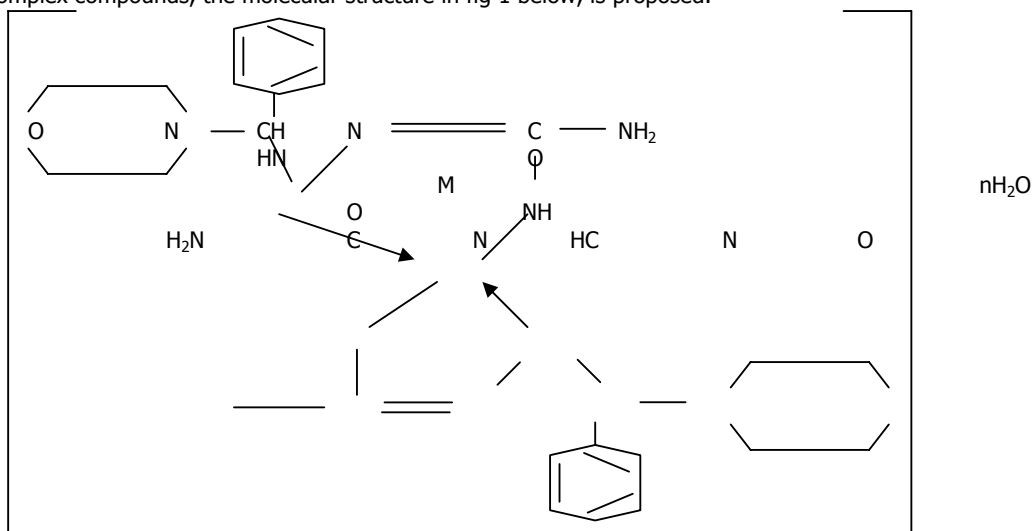


Fig 1: The proposed molecular structure of the complexes, where M is Mn(II) or Fe(II) and n, the number of water molecules.

Table 1: The Colour, Percentage Yield, melting point and decomposition temperature of the compounds

Complex/Compound	Colour	Melting Point (°C)	Decomposition temperature (°C)	point	Percentage yield (%)
Ligand	White	200	-		78.60
$[\text{MnL}_2] \cdot 4\text{H}_2\text{O}$	White	-	206		65.75
$[\text{FeL}_2] \cdot 2\text{H}_2\text{O}$	Brown	-	210		61.22
	Yellow				

Key: S = Soluble, SS = Slightly Soluble, Is = Insoluble

Table 2: Solubility test of the compounds in water and some common organic solvents

Compound	Water	Methanol	Ethanol	Acetone	Chloroform	Benzene	DMSO
Ligand	IS	S	S	SS	SS	SS	IS
$[\text{MnL}_2] \cdot 4\text{H}_2\text{O}$	IS	S	S	SS	SS	IS	SS
$[\text{FeL}_2] \cdot 2\text{H}_2\text{O}$	IS	S	S	SS	SS	IS	SS

Table 3: Conductivity Measurement of the Complexes in 10^{-3}M Methanol

Complexes	Concentration (mol/dm^3)	Specific conductivity ($\text{ohm}^{-1} \text{cm}^{-1}$)	Molar Conductivity ($\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$)
$[\text{MnL}_2] \cdot 4\text{H}_2\text{O}$	1×10^{-3}	3.38×10^{-6}	3.38
$[\text{FeL}_2] \cdot 2\text{H}_2\text{O}$	1×10^{-3}	6.90×10^{-6}	6.90

Table 4: Infrared Spectral Data of the ligand and its Metal (II) Complexes

Compound	$\nu(\text{C}=\text{N})$	$\nu(\text{H}-\text{O})$	$\nu(\text{C}=\text{C})$	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{N})$
Ligand	1599	3440-3560	1670	-	-
$[\text{MnL}_2] \cdot 4\text{H}_2\text{O}$	1565	3345-3580	1650	630-710	420-480
$[\text{FeL}_2] \cdot 2\text{H}_2\text{O}$	1600	3350-3540	1680	660-740	440-470

Table 5: Mole fraction and corresponding absorbance of manganese(II) complex

Mole fraction	Absorbance
0.1	0.04
0.2	0.14
0,3	0.27
0.4	0.34
0.5	0.45
0.6	0.56
0.7	0.69
0.8	0.50
0.9	0.43

Table 6: Mole fraction and corresponding absorbance of iron(II) complex

Mole fraction	Absorbance
0.1	0.04
0.2	0.10
0,3	0.16
0.4	0.27
0.5	0.34
0.6	0.45
0.7	0.49
0.8	0.34
0.9	0.20

Table 7: The stability constant and standard Gibb's free energy of the complexes

Compound	Stability constant	Gibb's free energy (KJmo ⁻¹)
[MnL ₂]4H ₂ O	1.24x10 ¹⁰	-65.79
[FeL ₂]2H ₂ O	8.21x10 ¹⁰	-60.35

Table 8: Determination of dissociation constant (pKa) of the Ligand

S/NO	Vol. of NaOH [cm ³]	pH	[H ⁺]	[OH ⁻]	[Na ⁺]	A _{tot} X 10 ⁻²	pka
1.	-	4.93	786x10 ⁻⁶	2.06x10 ⁻⁹	-	2.00	-
2.	0.5	5.0	6.69x10 ⁻⁶	2.42 x10 ⁻⁹	1.15 x10 ⁻³	1.20	6.14
3	1.0	5.02	6.39x10 ⁻⁶	2.54x10 ⁻⁹	2.29 x10 ⁻³	1.99	6.07
4	1.5	5.04	6.10x10 ⁻⁶	2.66 x10 ⁻⁹	3.42 x10 ⁻³	1.99	5.89
5	2.0	5.06	5.83x10 ⁻⁶	2.78x10 ⁻⁹	4.55 x10 ⁻³	1.98	5.67
6	2.5	5.06	5.83x10 ⁻⁶	2.78x10 ⁻⁹	5.66x10 ⁻³	1.98	5.63
7	3.0	5.07	5.70x10 ⁻⁶	2.85x10 ⁻⁹	6.80x10 ⁻³	1.97	5.62
8	3.5	5.08	5.57x10 ⁻⁶	2.91x10 ⁻⁹	7.91x10 ⁻³	1.97	5.42
9	4.0	6.01	6.54x10 ⁻⁷	2.48x10 ⁻⁸	9.02x10 ⁻³	1.96	6.25
10	4.5	6.01	6.54x10 ⁻⁷	2.48x10 ⁻⁸	1.01x10 ⁻²	1.96	6.15
11	5.0	6.02	6.39x10 ⁻⁷	2.53x10 ⁻⁸	1.12x10 ⁻²	1.95	6.07
12	5.5	6.03	6.24x10 ⁻⁷	2.60x10 ⁻⁸	1.23x10 ⁻²	1.95	5.97
13	6.0	6.05	5.96x10 ⁻⁷	2.72x10 ⁻⁸	1.34x10 ⁻²	1.94	5.87
14	6.5	6.05	5.96x10 ⁻⁷	2.72x10 ⁻⁸	1.45x10 ⁻²	1.94	5.75
15	7.0	6.06	5.83x10 ⁻⁷	2.78x10 ⁻⁸	1.56x10 ⁻²	1.93	5.60
16	7.5	6.08	5.57x10 ⁻⁷	2.91x10 ⁻⁸	1.66x10 ⁻²	1.93	5.46
17	8.0	6.11	5.19x10 ⁻⁷	3.12x10 ⁻⁸	1.77x10 ⁻²	1.92	5.21
18	8.5	6.12	5.08x10 ⁻⁷	3.20x10 ⁻⁸	1.88x10 ⁻²	1.92	4.62

The average dissociation constant, pKa = 5.40

Table 9: Determination of the number of coordinated ligands in Mn(II) complex

S/NO	Vol. of Liganate (cm ³)	Sodium pH	[H ⁺] x 10 ⁻⁴	[OH ⁻] x 10 ⁻¹¹	Log[A]	M _{tot} x 10 ⁻³	n
1.	4.2	3.25	3.76	4.31	-4.64	4.90	0.75
2.	4.4	3.28	3.51	4.62	-4.61	4.89	0.83
3	4.6	3.28	3.51	4.62	-4.61	4.89	0.91
4	4.8	3.29	3.43	4.73	-4.60	4.88	0.99
5	5.0	3.41	2.60	6,23	-4.47	4.88	1. 05
6	5.2	3.42	2.54	6.38	-4.46	4.87	1. 17
7	5.4	3.44	2.43	6.68	-4.44	4.87	1.23

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8	5.6	3.44	2.43	6.68	-4.44	4.86	1.29
9	5.8	3.46	2,32	6.99	-4.42	4.86	1.37
10	6.0	3.48	2.22	7.32	-4.40	4.85	1.45
11	6.2	3.50	2.12	7.66	-4.38	4.85	1.51
12	6.4	3.50	2.12	7.66	-4.38	4.84	1.60
13	6.6	3.51	2.07	7.84	-4.37	4.84	1.68
14	6.8	3.53	1.97	8.21	-4.35	4.84	1.76
15	7.0	3.54	1.93	8.40	-4.34	4.83	1.83
16	7.2	3.60	1.68	9.65	-4.28	4.83	1.90
17	7.4	3.60	1.68	9.65	-4,28	4.82	1.99
18	7.6	3.61	1.64	9.84	-4.27	4.82	2.05
19	7.8	3.63	1.57	10.3	-4.25	4.81	2.14
20	8.0	3.64	1.53	10.6	-4.24	4.81	2.17
21	8.2	3.64	1.53	10.6	-4.24	4.80	2.20
22	8.4	3.65	1.50	10.8	-4.23	4.80	2.31
23	8.6	3.65	1.50	10.8	-4.23	4.79	2.46
24	8.8	3.66	1.46	11.1	-4.22	4.79	2.55
25	9.0	3.66	1.46	11.1	-4.22	4.78	2.62
26	9.2	3.67	1.43	11.3	-4.21	4.78	2.70
27	9.4	3.67	1.43	11.3	-4.21	4.78	2.78
28	9.6	3.68	1.40	11.6	-4.20	4.77	2.85
29	9.8	3.68	1.40	11.6	-4.20	4.77	2.94
30	10	3.68	1.40	11.6	-4.21	4.76	3.01

The average number of ligands, n = 1.87

Table 10: Determination of the number of coordinated ligands in Fe(II) complex

S/NO	Volume of Sodium Liganate (cm ³)	pH	[H ⁺] x 10 ⁻⁴	[OH] x 10 ⁻¹¹	Log[A]	M _{tot} x 10 ⁻³	n
1	4,2	2.32	3.20	5.06	-6.00	4.90	1.33
2	4,4	2.34	3.06	5.30	-5.95	4.89	1.37
3	4.6	2.35	2.99	5.43	-5.92	4.89	1.45
4	4.8	2.36	2.92	5.55	-5.90	4.88	1,52
5	5.0	2.37	2.85	5.68	-5.87	4.88	1.58
6	5.2	2.39	2.73	5.95	-5,83	4.87	1.63
7	5.4	2.39	2.73	5.95	-5.83	4.87	1.72
8	5.6	2.40	2.66	6.09	-5.81	4.86	1.79
9	5.8	2.42	2.54	6.38	-5.76	4.86	1.85
10	6.0	2.44	2.43	6.68	-5.73	4.85	1.91
11	6.2	2.46	2.30	6.99	-5.68	4.85	1.95
12	6.4	2.48	2.22	7.32	-5.65	4.84	2.02
13	6,6	2.48	2.22	7.32	-5.65	4.84	2.10
14	6.8	2.51	2.07	7.84	-5.60	4.84	2.15
15	7.0	2.52	2.02	8.03	-5.58	4.83	2.21

Table 10 continue

16	7.2	2.56	1.84	8.80	-5.51	4.83	2.26
17	7.4	2.61	1.64	9.87	-5.44	4.82	2.31
18	7.6	2.72	1.27	12.7	-5.28	4.82	2.29
19	7.8	2.73	1.25	13.0	-5.27	4.81	2.38
20	8.0	2.73	1.25	13.0	-5.27	4.81	2.46
21	8.2	2.73	1.25	13.0	-5.30	4.80	2.55
22	8.4	2.77	1.14	14.3	-5.22	4.80	2.59
23	86	281	1.04	156	-5.17	4.79	2.66
24	8.8	2.81	1.04	15.6	-5.17	4.79	2.74
25	90	2.83	0.99	16.4	-5.14	4.78	2.80
26	9.2	2.83	0.99	16.4	-5.14	4.78	2.89
27	9.4	2.85	0.95	17.2	-5.12	4.78	2.96
28	9.6	2.85	0.95	17.2	-5.12	4.77	3.03
29	9.8	2.85	0.95	17.2	-5.12	4.77	3.12
30	10	2.85	0.95	17.2	-5.12	4.76	3.20

The average number of ligand, n = 2.22

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