Thermogravimetric and Gas Chromatographic Studies of Copper(II) and Nickel(II) Chelates of Meso and Dl-Bis-(Isovalerylacetone)Stilbenediimine.

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(Received 12th July, 1984)

Summary: Copper(II) and nickel(II) chelates of two tetradentate Schiff bases bis(isovalerylacetone)meso-stilbenediimine(meso-SiA_2) and bis(isovaleryl-acetone)dl-stillbenediimine(dl-SiA_2) have been prepared and characterized using IR, NMR and mass spectroscopic techniques. The metal complexes have been assessed spectrophotometrically and their potentialities as analytical reagents have been evaluated. TGA, DTA and DSC of these complexes indicate that the metal complexes are sufficiently volatile and thermally stable at high temperature. The metal complexes can be gas chromatographed on OV 101, 3% on chromosorb 80-100 mesh size. Detection limit, calibration range and separation of dl and meso geometrical isomers are reported. The nickel chelates show greater sensitivity and low detection limits than the corresponding copper complexes at ng levels.

Introduction

It is well recognised that tetradenate β-ketoamines form coloured metal complexes with favourable features in terms of thermal stability and gas chromatographic applications for the analysis of divalent transition metal ions [1-8]. Most of the work has been concentrated towards β-ketoamines derived from the condensation of β-diketones with ethylenediamine and propylenediamine, but relatively less work has been reported on the corresponding use of stilbenediamine [9-12]. Therefore, two new schiff bases derived from the condensation of isovalerylacetone and meso- and dl-stilbenediamine have been reported to assess them as complexing and gas chromatographic reagents for the analysis of metal ions.

Experimental

Preparation of the Reagents

Bis(isovalerylacetone)meso-stilbenediimine(meso-SiA_2):

Freshly distilled isovalerylacetone (2.9 g, 0.02 mole) was heated together with (2.1 g, 0.01 mole) of meso-stilbenediamine on a water bath for 30 minutes. The reaction mixture was left overnight and the precipitate was washed with ether and recrystallised from ethanol.

Bis(isovalerylacetone)dl-stilbenediimine (dl-SiA_2):

Isovalerylacetone (2.9 g 0.02 mole) and dl-stilbenediimine (2.1 g, 0.01 mol) were mixed together and the

mixture was shaken for 5 minutes with occasional cooling. The reaction mixture was allowed to stand at room temperature for a few days and the reagent slowly precipitated out as a solid mass. The precipitate was washed with ether followed by n-hexane and recrystallized from ethanol.

Metal Chelates

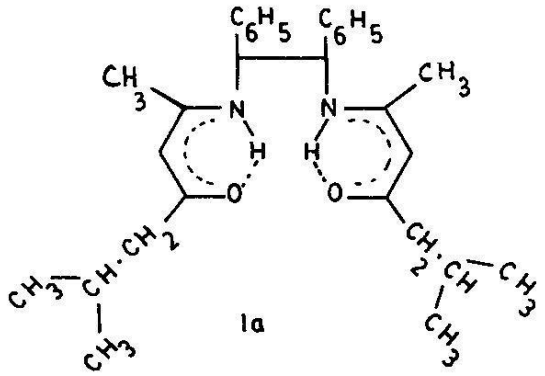
Equimolar solution of copper acetate and nickel acetate in ethanol was slowly added to the refluxing solution of the reagents in ethanol and was refluxed for 30 minutes. The mixture was allowed to cool and the precipitate was recrystallised from ethanol and dried at 110°C. Meso SiA_2Ni gave the light wooly mass and its micro-analysis corresponds to the molecular formula $C_{30}H_{38}N_2O_2Ni.H_2O$. However, when the complex was repeatedly recrystallized from ethanol, it slowly changed to dark coloured crystals, the micro analysis of which agreed to the molecular formula $C_{30}H_{38}N_2O_2Ni$. The results of elemental micro analysis with melting points and % yield of compounds are summarized in Table 1.

Elemental micro-analysis was carried out by Elemental Micro-Analysis Ltd., U.K. Metal content of the complexes was determined using Hitachi 180-50 Atomic Absorpition Spectrometer, IR spectra were recorded on Hitachi 260-50 IR Spectrophotometer in the range of 4000-250 cm^{-1}. PMR spectra were recorded at the H.E.J. Research Institute of Chemistry, Karachi University.

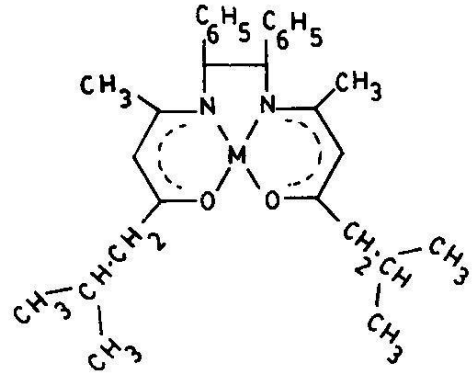
The TG, and DTA were recorded with stanton TG-77 Thermal Analyser from Elemental Micro-Analysis Ltd., U.K. at the scan rate of 15-20°C/min in flowing nitrogen atmosphere at the rate of 20Cm^3/min with 5-10 mg of sample. The Hitachi 163 Gas Chromatograph equipped with flame ionization detector was used. Stainless steel column 2mx3mm and 3mx3mm packed with OV101, 3% on WHP Chromosorb 80-100 mesh size, OV1, 3% WHP chromosorb 80-100 mesh size, OV1, 3% Uniport HP 60-80 mesh size, Dexil 400 GC 2%, on Uniport HP 60-80 mesh size were used throughout the study. All columns were conditioned at the appropriate temperature before analysis.

Results and Discussion

The analysis of dried copper and nickel chelates indicated that the reagent is attached as binegative anion



Ia



M = cu(II) & Ni(II)

Ib

Fig.1: (a) and Ib. structural diagrammes of reagents and their metal chelates.

Table-1: Results of the Elemental Micro analysis and % yield of Compounds

No.	Name of the Compound	Melting point	% yield	Molecular formula	% expected C	H	N	M	% Found C	H	N	M
1.	Bis(isovalerylacetone)-meso-stilbenediimine	160	80	$C_{30}H_{40}N_2O_2$	78.26	8.67	6.08	-	77.7	8.75	6.01	-
2.	Bis(isovalerylacetone)-dl-stilbenediimine.	107	85	$C_{30}H_{40}N_2O_2$	78.26	8.67	6.08	-	78.23	8.66	6.09	-
3.	Bis(isovalerylacetone)-meso-stilbenediimine copper(II)	168	70	$C_{30}H_{38}N_2O_2Cu(II)$	69.02	7.28	5.36	12.18	68.96	7.28	5.26	11.75
4.	Bis(isovalerylacetone)-meso-stilbenediimine nickel(II)	174	60	$C_{30}H_{38}N_2O_2$ $H_2ONi(II)$	67.32	7.45	5.23	10.97	67.50	7.23	5.14	11.20
5.	Bis(isovaleryacetone)-meso-stilbenediimine-nickel(II).	170	25	$C_{30}H_{38}N_2O_2Ni(II)$	69.6	7.35	5.41	11.36	69.45	7.59	5.58	11.0
6.	Bis(isovalerylacetone)-dl-stilbenediimine copper(II)	234	60	$C_{30}H_{38}N_2O_2Cu(II)$	69.02	7.28	5.36	12.18	69.25	7.35	5.36	11.87
7.	Bis(isovalerylacetone)-dl-stilbenediimine Nickel(II).	230	65	$C_{30}H_{38}N_2O_2Ni(II)$	69.6	7.35	5.41	11.36	69.56	7.41	5.39	11.13

to metal ion only, except in meso-$SiA_2Ni.H_2O$ which precipitate out initially with a water molecule. However, on repeated recrystallization it loses the water molecule.

Mass spectra of the ligands indicated relatively small intensities of the molecular ion peaks at m/e 460 (2.4%). These are indicative of the ease of the fragmentation of the compounds, and this may reflect the number of heteroatoms present in each molecule. The major fragmentation reactions are similar to those observed previously for the related compounds [13], and the main fragmentation path way of the ligands involves the loss of half of the ligand at m/e 230 (100%) by the cleavage of bridge ethylene groups.

Ueno and Martell [14] have suggested on the basis of IR studies of bis(acetylacetone)ethylenediimine that the reagent exists predominantly in ketoamine form. This has been supported by Dudeck [15], Pasini [16] and Lindoy [13] on the basis of IR, NMR and mass spectral data. The results of IR agreed with earlier reports with related compounds. Two absorption regions have a bearing on structural problem. First absorption above 3100 cm^{-1}. The ligand dl-SiA_2 shows two peaks one strong band at 3565 cm^{-1} and other of medium intensity at 3340 cm^{-1}, whereas meso-SiA_2 shows a band of weak intensity at 3160 cm^{-1}, which could be assinged to chelated NH...O group. However the bands disappear in copper and nickel chelates due to complexation. Secondly, the region from 1690-1490 cm^{-1}, where the reagents show three to four bands. The assignment of these bands should be considered as important, as C=O, C=C, C=N and phenyl ring vibrations may all be expected near 1600 cm^{-1}. In fact both C-O and C-N bonding would be expected to have partial double bond character assuming pseudo-aromatic ring. The bands at 1610 cm^{-1} and 1612 cm^{-1} in dl-SiA_2 and meso-SiA_2 respectively is assigned to hydrogen bonded, conjugated C=O group. A band of weak to medium intensity observed in the spectrum of dl-SiA_2 at 1690 cm^{-1} could be assigned to C=O group. However, these bands disappear and the relative intensity of the absorption near 1500 cm^{-1} increase significantly in copper and nickel chelates upon complexation. The bands observed in spectra of copper and nickel complexes of meso-SiA_2 and dl-SiA_2 at 535, 545, 520 and 525 cm^{-1} respectively are assigned due to metal ligand vibrations.

The IR spectra of meso-$SiA_2Ni.H_2O$ and meso-SiA_2Ni complexes showed similar pattern except the former shows broad band at 3450 cm^{-1} due to -OH vibrations.

The PMR spectra of the ligands and a diamagnetic nickel chelate indicates the multiplets in the spectrum of the reagent between δ 4.7-4.9 ppm and δ 11.75-11.85 ppm for the bridge -CH proton and NH...O group, respectively. The former changed into singlet at δ 4.15 ppm and the latter disappeared in dl-SiA_2Ni due to complexation and supports that the dianion of the ligand is bonded to the metal ion. A singlet observed in the spectra of the ligands and nickel chelate between δ 4.8-4.95 ppm. corresponding to two protons, is assigned to the vinylic protons.

The isomeric ligands dl and meso differ only in the spatial arrangement of the protons and the phenyl groups on the ethylene bridge. The methyl groups in both of the isomers are near the π clouds of the adjacent phenyl groups and cause down field of their response. However in dl form these methyl groups are on the average farther from the phenyl groups and hence affected to a much lesser extent by the π cloud than the meso form. Thus the methyl signal in dl isomer appears at δ 1.84 ppm slightly higher than meso at δ 1.5 ppm.

Similarly NH...O experience deshielding due to the phenyl rings and shows the resonance at δ 11.85 and 11.75 ppm for dl and meso isomers respectively as compared to bis(isovalerylacetone)ethylenediimine at 11.1 ppm [13]. The replacement of proton from the bridge $-CH_2$ group from $eniA_2$ ligand with phenyl group results the signal of remaining bridge -CH protons at δ 4.7 and δ 4.1 ppm in dl and meso-isomers respectively as compared to $eniA_2$ at δ 3.43 ppm due to the π clouds of phenyl group.

Spectrophotometric Studies

The formation of the coloured complexes of copper(II) and nickel(II) with the reagents prompted their exploration as spectrophotometeric reagents for the quantitative determination of copper and nickel. The results of absorptiometric data are summarized in Table 2. The copper complexes are bluish to purple in colour, but the values of molar absorptivity indicate that the copper complexes are relatively less sensitive for quantitative purposes and obey Beer's law at mg/ml levels. The nickel (II) complexes show two bands in the visible region and yellow colours show higher sensitivity and obey the Beer's law at their respective wavelengths of maximum absorbances at μg/ml levels.

Thermogravimetric Studies

A prerequisite for the effective applications of a reagent in GLC is that it should be sufficiently volatile and thermally stable at working temperatures. The volatility of metal complexes was therefore checked by sublimating the complexes in sublimating apparatus immersed in an oil bath. The sublimates of the copper and nickel complexes were collected on cold finger between 190-210°C at 2.5 mm pressure.

TG of crystalline dl-SiA_2Cu shows single loss between 200-300°C with maximum rate at 270°C and leaves 3-7% green residue. DSC indicates melting point at 255°C followed by vaporisation endotherns at 270°C. TG of crystalline dl-SiA_2Ni shows single complete loss between 216-340°C with maximum rate at 311°C. DTA indicates melting point at 226°C followed by the vaporisation endotherm at 291°C with opaque yellow sublimate. TG of crystalline meso-SiA_2Cu shows single complete loss between 192-330°C with maximum rate at 300°C. DTA indicates melting point at 163°C followed by vaporisation endotherm at 330°C. TG of red brown crystalline meso-SiA_2Ni shows loss of 93% between 192-400°C, with a maximum rate at 280°C and 75% loss by 330°C. DTA indicates melting endotherm at 170°C followed by vaporisation endotherm upto 550°C.

TG, DTA and DSC of the copper and nickel complexes shows that all the four samples appear to melt without decomposition at specified temperatures and mostly vaporised

Table-2: Quantitative Absorptiometric data of copper(II) and nickel(II) complexes.

Compound	Metal ion	Solvent	Color	λ_{max} nm	ε l. mole^{-1} cm^{-1}	Solution Stability	Calibration range
1. Bis(isovalerylacetone)-meso-stilbenediimine	-	Chloroform	-	325 202	42923 5807	-	-
	Ni(II)	Chloroform	Yellow	570 362	249 9639	week	Beer's law obeyed in the range 8.0-80.0 µg/ml of complex, corresponding to the 0.909-9.09 µg/ml of nickel at 362 nm.
	Cu(II)	Chloroform	Blue	560	225	week	Obeys Beer's law in the range of 0.32-2.56 mg/ml of complex corresponding to 39-312 µg/ml of copper at 560 nm.
2. Bis (isovalerylacetone)-dl-stilbenediimine.	-	Chloroform	- 220	312 5031	39445	-	-
	Ni(II)	Chloroform	Yellow	379 362 567	7382 6742 83	week	Beer's law is obeyed over 8.0-80 µg/ml of complex,corresponding to 0.9-9.0µg/ml of nickel at 380 nm.
	Cu(II)	Chloroform	Blue	545	195	week	Beer's law is obeyed over 0.32-2.56 mg/ml, corresponding to 39-312 µg/ml of copper.

unchanged below 350°C. However meso-SiA_2Ni and dl-SiA_2Cu leave certain residue behind. Thus the results are quite encouraging that complexes are reasonably volatile and thermally stable. The reagents could be used for the quantitative determinations of metal ions with the aid of GLC effectively.

Gas Chromatography

Because of high temperature required for volatilisation of copper and nickel complexes as reflected from TG curves, suitable liquid phase OV101, 3% on Chromosorb, OV1, 3% on Chromosorb, OV1, on Uniport and Dexil 400GC, 2% on Uniport were selected to allow high operating temperatures. Stainless steel column 2mx3mm packed with OV101, 3% on Chromosorb 80-100 mesh size gave satisfactory results with symmetrical peaks with good base line return. The flow of the carrier gas and column temperature were optimised (Table 3. Fig. 3 and 4).

When a mixture of copper and nickel chelates of dl-SiA_2 or meso-SiA_2 is injected on the column at the temperature optimised for individual reagent, no separation between copper and nickel chelate was achieved. The column length was increased and other stationary phases, OV1, 3% on chromosorb, OV1, 3% on Uniport, Dexil 400, GC 2% on Uniport and Apiezon 'L' 15% on Uniport were tried without much success and each time slightly broader single peak was observed for a mixture of copper and nickel complexes. However, when a mixture of metal complexes of isomers dl-SiA_2 and meso-SiA_2 was injected on OV101, 3% on chromosorb column at a column temperature of 255°C complete separation of the isomers was achieved.

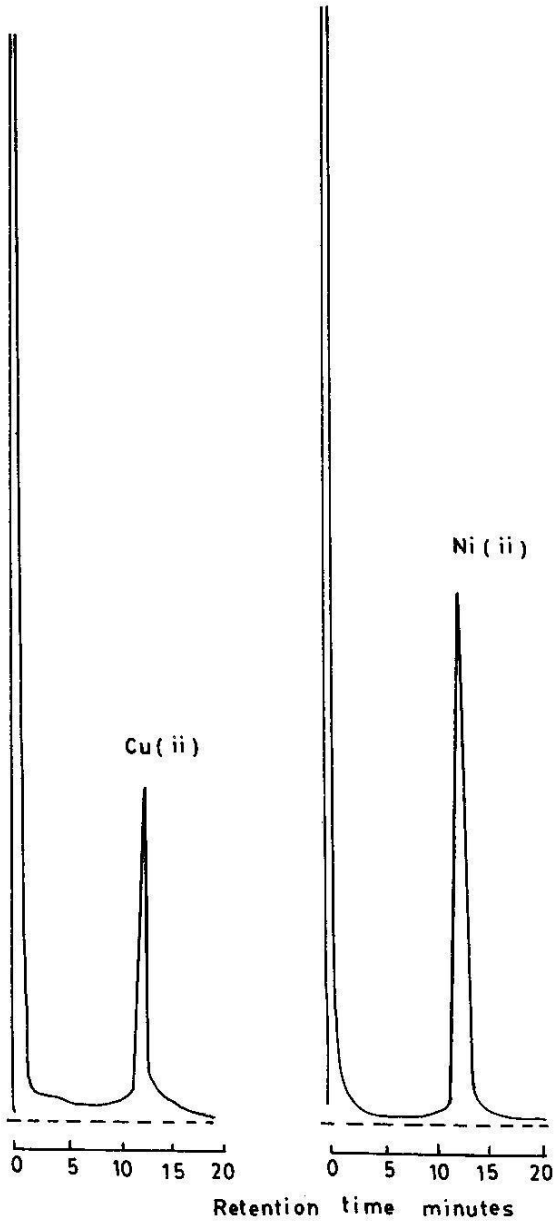


Fig.3: Representative chromatogram of copper (II) and nicke(II) chelates of dl-SiA_2, on 2mx3mm stainless steel column packed with 3% OV-101 on chromosorb WHP 80-100 mesh size N_2=25Cm^3 min^{-1}. Column temp: 260°.

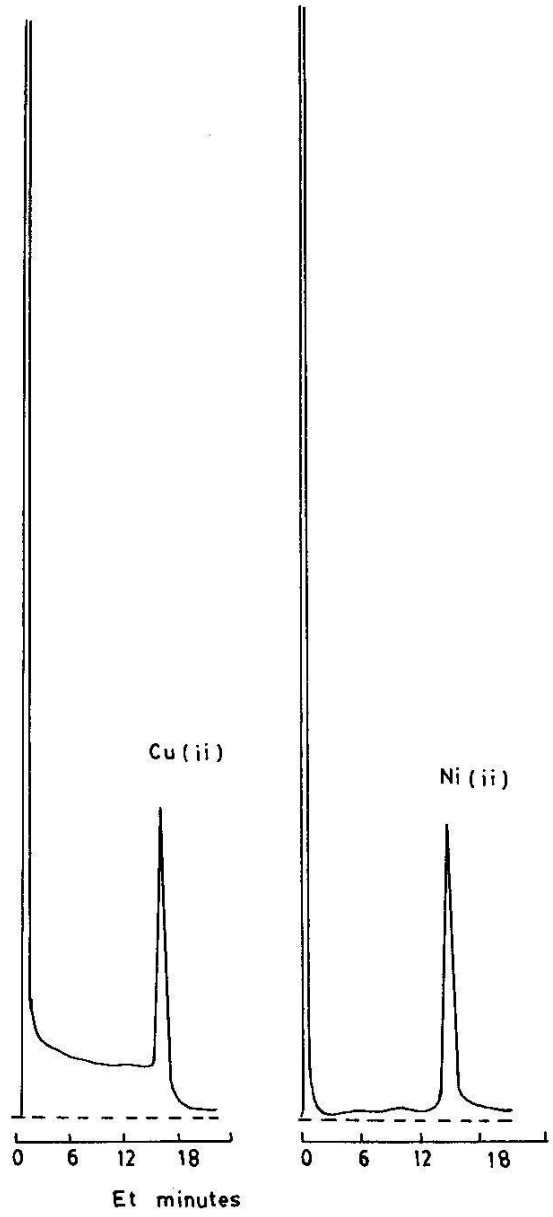


Fig.4: Representative chromatograms of copper(II) and nickel(II) chelates of meso-SiA_2 on 2mx3mm stainless steel column packed with 3% OV-101 on chromosorb WHP 80-100 mesh size. N_2=28Cm^3/min column temp. 265°C.

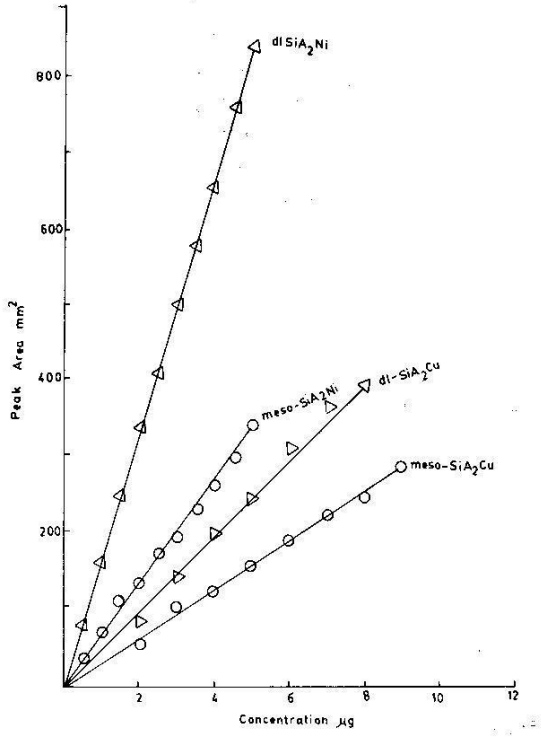


Fig.5: Quantitative response curves for copper(II) and Ni(II) chelates of meso and dl-SiA_2 on 2mx3mm stainless steel column packed with 3% OV-101 on chromosrob WHP 80-100 mesh size.

To check if the amount of the complex eluted is quantitative with amount injected the solution of known amounts of the complex in acetone was injected and the average of the peak area of at least two injections were measured by multiplying the peak height with the width at half hieght and straight line calibration curve was obtained for each of the complex, with average deviation within ± 2.5%. The calibration ranges with detection limits are summarized in Table 3.

The calibration curves in (fig 5) indicate that the nickel complexes of both of the ligands are more sensitive

Table-3: Quantitative Gas Chromatographic data of copper(II) and nickel(II) complexes.

Complexing Reagent	Metal Complex	Retention time in Seconds	Flow rate of N_2, cm^3/min	Column T°C	Calibration range	Detection Limit rang
1. Bis(isovalerylacetone)-dl-stilbenediimine	Ni(II)	690	25	260	0.5-5.0 µg of complex corresponding to 0.057-0.57 µg of nickel.	0.1 µg of complex corresponding to 11 ng of nickel.
	Cu(II)	685	25	260	2-9 µg of complex corresponding to 0.24-1.09 µg of copper.	0.4 µg of complex corresponding to 48ng of copper.
2. Bis(isovalerylacetone)-meso-Stilbendiimine	Ni(II)	970	28	265	0.5-5.0 µg of complex corre-esponding to 0.057-0.5 µg of nickel.	0.2 µg of complex corresponding to 23 ng of nickel.
	Cu(II)	960	28	265	2-9 µg of complex corresponding to 0.24-1.09 µg of copper.	0.6 g of complex corresponding to 73 ng of copper.

than corresponding copper complexes. Moreover copper and nickel complexes of dl-SiA_2 ligand show higher sensitivity and lower detection limit than corresponding metal complexes of meso-SiA_2 isomer. Finally the copper complex of meso-SiA_2 is least sensitive among the series.

Conclusion

The ligands and their copper and nickel complexes are prepared by simple synthetic routine and characterised using spectroscopic technique. The colour of nickel complexes show reasonable sensitivity, but copper complexes lack sufficient sensitivity spectrophotometrically. The copper and nickel complexes of both the reagents show good thermal stability and volatility idealy suited for gas chromatographic applications. The copper and nickel complexes show excellent sensitivity with detection limits at ng levels particularly copper and nickel complexes of dl-SiA_2 gas chromatographically, but failed to separate copper and nickel complexes in a mixture under present conditions.

Acknowledgement

Thanks are due to Pakistan Science Foundation for financing the Project.

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