

subjected to Group II plasma, indicates the presence of some factors in onion extract which help for retaining the normal shape of erythrocytes. To observe the effect of Group III plasma on Group II erythrocytes, these were mixed and incubated by similar method as mentioned above. Crenation of the cells disappears and they closely resemble normal control cells, as shown in Fig. 5.

Recovery of the cells from crenation indicates the presence of some factors in Group III plasma which counterbalances the cholesterol effect and this plasma behaves similar to the normal control plasma.

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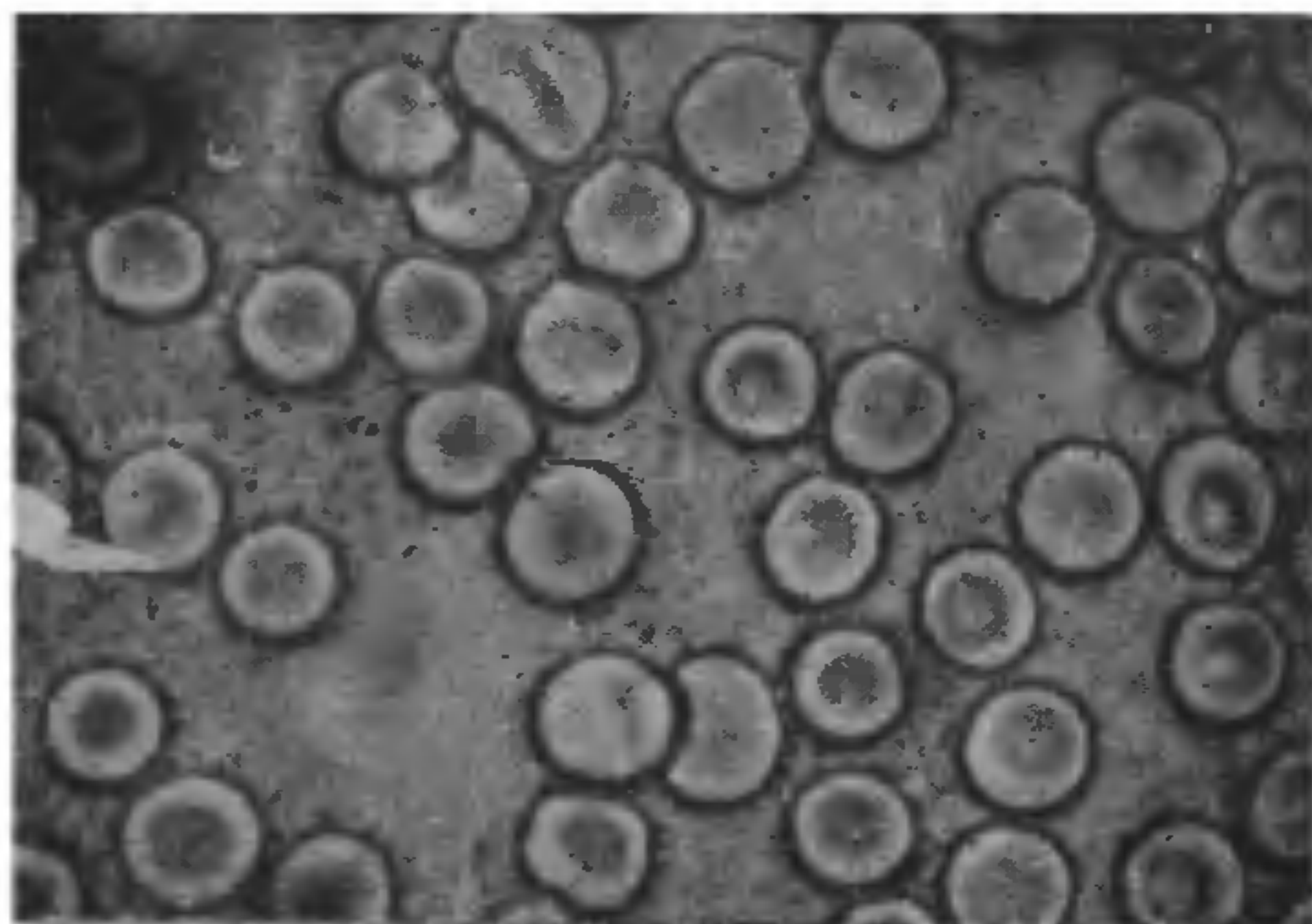


FIG. 5. Erythrocytes of Group II, after incubation with plasma of Group III, show the recovery from crenation and appear similar to normal control cells.

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## 4-DIMETHYLAMINO PYRIDINE-1-OXIDE COMPLEXES OF LANTHANIDE PERCHLORATES

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### ABSTRACT

Adducts of Lanthanide Perchlorates with 4-dimethyl amino pyridine-1-oxide (DMPO) have been synthesized for the first time and characterized by analysis, electrolytic conductance, infrared, proton NMR and electronic spectral data. The complexes have the compositions  $\text{Ln}_2(\text{DMPO})_{13}(\text{ClO}_4)_6$  ( $\text{Ln} = \text{La, Pr, Nd and Sm}$ ) and  $\text{Ln}(\text{DMPO})_6(\text{ClO}_4)_3$  ( $\text{Ln} = \text{Gd, Tb, Dy, Ho and Yb}$ ). A tentative coordination number of seven for the complexes of the type  $\text{Ln}_2(\text{DMPO})_{13}(\text{ClO}_4)_6$  and of six for the type  $\text{Ln}(\text{DMPO})_6(\text{ClO}_4)_3$  have been assigned.

### 2 INTRODUCTION

THE study of the coordination compounds of a variety of lanthanide salts, with pyridine-N-oxide (PyO) and methyl substituted pyridine-N-oxides has shown that the substitution of the methyl group at 3 and 4 positions of the PyO moiety has no influence on the coordination number around the lanthanide ions<sup>1-3</sup>. We have now initiated a systematic programme involving adducts of lanthanide salts with pyridine-1-oxides having substituents other than the methyl group. We report in this paper the preparation and characterization of the complexes of lanthanide perchlorates with 4-dimethylamino pyridine-1-oxide

with an attempt to compare the complexes with those of 4-MePyO<sup>3</sup>, 4-chloro PyO and 4-nitro PyO<sup>4</sup>. The complexes have been characterized by analysis, conductance, IR, NMR and electronic spectra.

### 2. EXPERIMENTAL

#### 2.1. Preparation of the Ligand

4-Nitro pyridine-1-oxide was prepared by nitration of pyridine-1-oxide as described by Katritzky<sup>5</sup>. 4-Chloropyridine-1-oxide was obtained by the reaction of 4-nitropyridine-1-oxide with acetyl chloride according to the method given by Ochiai<sup>6</sup>. 4-Dimethylamino-pyridine-1-oxide was now prepared by reacting

dimethylamine with 4-chloro pyridine-1-oxide in a sealed tube<sup>7</sup> and purified by crystallization from ethylacetate (m.p. 222° C, lit. value 223.5° C).

### 2.2. Preparation of the Complexes

Hydrated lanthanide perchlorate (0.6 mM) dissolved in ethyl acetate (10 ml) was added drop by drop to a solution of DMPO (6 mM) in chloroform (5 ml) with stirring. A solid precipitated. As the complex was soluble in chloroform ethylacetate (5 ml) was added for complete precipitation and the mixture was boiled on a water bath with stirring. The complex was filtered, washed 3–4 times with hot ethyl acetate and finally with ether and dried over phosphorus pentoxide in a vacuum desiccator.

### 2.3. Analysis

The metal in the complexes was estimated by complexometric titration with EDTA using xylenol orange as indicator<sup>8</sup>. Perchlorate was determined by gravimetric precipitation with nitron<sup>9</sup>. The ligand DMPO was analysed spectrophotometrically at 294 nm.

### 2.4. Physical Methods

The infrared spectra of the ligand and the complexes in nujol mull in the region 400–4000 cm<sup>-1</sup> were recorded on a Carl-Zeiss-UR-10 infrared spectrophotometer.

Proton NMR spectra of the lanthanum complex and the ligand were recorded on a Varian T-60 instru-

ment using CH<sub>3</sub>CN as solvent and TMS as the internal standard.

Electronic spectra of Nd and Ho complexes in acetonitrile solutions were recorded in the region 350–700 nm on a Unicam SP 700 spectrophotometer. The solid state spectra of the complexes in nujol mull were obtained on the same instrument.

Conductance measurements in acetonitrile and in nitrobenzene were carried out in a Siemen's conductivity bridge using an immersion cell (type LTA). The concentrations of the solutions used were of the order of 0.001 M.

## 3. RESULTS AND DISCUSSION

The complexes of 4-DMPO are non hygroscopic and soluble in methanol, acetone, acetonitrile, chloroform and nitrobenzene. They are however, insoluble in benzene, carbon tetrachloride and ethyl acetate. The colours of the complexes are the same as those of the parent lanthanide salts.

Analytical and conductance data are given in Table I. The analytical data show that the complexes have the formulae Ln<sub>2</sub>(DMPO)<sub>13</sub>(ClO<sub>4</sub>)<sub>6</sub> (Ln = La, Pr, Nd and Sm) and Ln(DMPO)<sub>6</sub>(ClO<sub>4</sub>)<sub>3</sub> (Ln = Gd, Tb, Dy, Ho and Yb).

TABLE I  
Analytical and Molar conductance data

Complexes	% Metal	% DMPO	% ClO <sub>4</sub>	$\Lambda_m^+$	
				CH <sub>3</sub> CN	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>
La <sub>2</sub> (DMPO) <sub>13</sub> (ClO <sub>4</sub> ) <sub>6</sub>	10.28 (10.42)	68.14 (67.23)	21.46 (22.38)	392.00	69.39
Pr <sub>2</sub> (DMPO) <sub>13</sub> (ClO <sub>4</sub> ) <sub>6</sub>	10.43 (10.54)	65.90 (67.14)	..	398.51	70.14
Nd <sub>2</sub> (DMPO) <sub>13</sub> (ClO <sub>4</sub> ) <sub>6</sub>	10.70 (10.76)	65.41 (66.94)	..	391.70	69.81
Sm <sub>2</sub> (DMPO) <sub>13</sub> (ClO <sub>4</sub> ) <sub>6</sub>	11.30 (11.19)	67.12 (66.53)	22.31 (22.17)	398.80	69.52
Gd <sub>2</sub> (DMPO) <sub>13</sub> (ClO <sub>4</sub> ) <sub>6</sub>	12.20 (12.25)	65.73 (64.48)	22.26 (22.08)	406.50	69.16
Tb(DMPO) <sub>6</sub> (ClO <sub>4</sub> ) <sub>3</sub>	12.28 (12.36)	65.26 (64.43)	..	390.10	69.46
Dy(DMPO) <sub>6</sub> (ClO <sub>4</sub> ) <sub>3</sub>	12.44 (12.60)	64.81 (64.22)	..	400.10	69.74
Ho(DMPO) <sub>6</sub> (ClO <sub>4</sub> ) <sub>3</sub>	12.76 (12.77)	65.15 (64.13)	..	396.30	70.21
Yb(DMPO) <sub>6</sub> (ClO <sub>4</sub> ) <sub>3</sub>	13.23 (13.31)	64.59 (63.72)	22.10 (22.57)	397.61	69.92

+ Molar Conductance — Ohms<sup>-1</sup> cm<sup>2</sup> mole<sup>-1</sup> for monomer.  
(Figures in parenthesis are calculated values).



TABLE II  
IR and NMR spectral data

(a) IR spectra of DMPO complexes in Nujol mull											
DMPO [DMPOH] <sup>+</sup> (ClO <sub>4</sub> ) <sup>-</sup>	La	Pr	Nd	Sm	Gd	Tb	Dy	Ho	Yb	Assignments	
1225s	1230s	1235s	1235s	1240s	1235s	1235vs	1235s	1235s	1235s	1240s	$\nu_{N-O}$
835s	835s	838s	840s	840m	840s	840s	840s	840s	840s	840s	$\delta_{N-O}$
1645s	1650s	1655s	1655s	1660s	1650s	1650s	1650s	1650s	1650s	1650s	Ring stretching
	1100vs	1100vs	1100vs	1100vs	1100vs	1100vs	1100vs	1100vs	1100vs	1100vs	$\nu_3$ ClO <sub>4</sub> <sup>-</sup>
	625m	625m	625m	625m	625m	625m	625m	625m	625m	625m	$\nu_4$ ClO <sub>4</sub> <sup>-</sup>

(b) Proton NMR spectra for La complex in CH <sub>3</sub> CN (TMS int. stand. chemical shift in $\delta$ )			
Sigal	DMPO	La <sub>2</sub> (DMPO) <sub>13</sub> (ClO <sub>4</sub> ) <sub>6</sub>	
2, 6-H	2.35	2.05	( $\Delta = +7$ Hz)
3, 5-H	3.42	3.52	( $\Delta = -6$ Hz)

vs = very strong, s = strong, m = medium.

Molar conductance data in acetonitrile and in nitrobenzene are in the range expected for 1:3 electrolytes in these solvents<sup>10</sup>. This suggests that the perchlorate groups in complexes are ionic.

Infrared frequencies for the ligand and the complexes along with their assignments are presented in Table II. The characteristic features of the IR spectra are (1) a shift in the N-O stretching frequency from 1225 cm<sup>-1</sup> in the ligand to 1235 cm<sup>-1</sup> in the complexes, (2) an increase in the  $\delta_{N-O}$  and the ring stretching vibrations of the ligand, and (3) retention of the characteristic vibrations of the ionic perchlorate group.

DMPO on protonation at the N-oxide shows a positive shift of  $\nu_{N-O}$  by 5 cm<sup>-1</sup>. Field *et al.*<sup>11</sup> have found a positive  $\nu_{N-O}$  shift by 1 cm<sup>-1</sup> in (Nb<sub>6</sub>Cl<sub>12</sub>) Cl<sub>4</sub> (DMPO)<sub>4</sub>. These are in line with the present observation. The shift of  $\delta_{N-O}$  and ring stretching bands to higher frequencies upon complexation indicate a flow of electron density from the ring to the metal ion. The  $\nu_3$  mode (1100 cm<sup>-1</sup>) and  $\nu_4$  mode (625 cm<sup>-1</sup>) of the ClO<sub>4</sub> group remain unsplit showing that the perchlorate groups have the T<sub>d</sub> symmetry. This is in line with the 1:3 electrolytic conductivity of the complexes.

The proton NMR spectra of the ligand are sharp and well resolved. The doublets occurring at 2.35  $\tau$  and 3.42  $\tau$  in the ligand correspond to the signals of  $\alpha$  and  $\beta$  protons respectively. The  $\alpha$ H and  $\beta$ H signals which are sharp and well resolved, occur at 2.05  $\tau$  and 3.52  $\tau$ , respectively in the diamagnetic La<sup>3+</sup> complex. The positive shift of the  $\alpha$  proton signal (+7 Hz) in the complex arises from the deshielding of the  $\alpha$  protons due to the flow of electron density from the ligand to the metal ion on coordination. The negative shift of the  $\beta$ H signal (-6 Hz) indicates shielding at  $\beta$  protons which is probably due to the drainage of the electron density from the dimethyl amino group to the metal on complexation.

The shapes of the hypersensitive electronic spectral bands have been found to be dependent on the coordination number around the +3 lanthanide ions. All the bands shift to lower energy compared to those of aquo ions, a feature found in the spectra of lanthanide complexes involving most of the ligands. This is due to the nephelauxetic effect<sup>12</sup>. The shapes of the hypersensitive bands  $^4I_{9/2} \rightarrow ^4G_{5/2}$ ,  $^2G_{7/2}$  and  $^5I_8 \rightarrow ^5G_4$ ,  $^6F_1$  for Nd<sup>3+</sup> and Ho<sup>3+</sup> DMPO complexes respectively in the solid state and in the solution resemble those of seven and six coordinate complexes studied by Karaker<sup>13</sup>.

## 4. CONCLUSION

The proton NMR spectra along with IR data for the complexes indicate the coordination of the ligand through the oxygen of the N-O group. The conductivity data for all the complexes along with the electronic spectral data for  $\text{Nd}^{+3}$  and  $\text{Ho}^{+3}$  complexes point to a coordination number of seven in the complexes of La, Pr, Nd and Sm and of six in the complexes of Gd, Tb, Dy, Ho and Yb.

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## MASS SPECTRAL STUDIES ON SCHIFF BASE COMPLEXES OF GERMANIUM (IV)

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## ABSTRACT

Mass spectral fragmentation of bis [N-(3-hydroxy-1-propyl)-2-hydroxy-1-naphthalaldiminato] germanium (IV) has been studied at 70 eV and high resolution. Suitable fragmentation schemes have been suggested and these are in most of the cases supported by the appropriate metastable peaks.

## INTRODUCTION

THE mass spectra of Schiff base complexes have not been extensively studied. In those cases where mass spectra have been reported<sup>1-4</sup>, it has been possible to assign molecular weights to the various species in the gaseous phase, and further to examine the fragmentation patterns for being used in the structure elucidations.

Lara *et al.*<sup>5</sup>, have recorded the mass spectral studies of some of the Ni(II) complexes, whereas Banfield<sup>6</sup> has reported the mass spectra of the Schiff base complexes of Cobalt(II). However, the literature does not record any reference on the mass spectral fragmentation of the Schiff base complexes of germanium. In the present paper, we report the results of the mass spectral fragmentation of bis [N-(3-hydroxy-1-propyl)-2-hydroxy-1-naphthalaldiminato] germanium(IV).

## EXPERIMENTAL

Mass spectrum was recorded using a MS-30 Mass spectrometer at 70 eV. The source was maintained at 210° C and the compound introduced as a solid

using a direct insertion probe. The compound was prepared by the standard method reported earlier.<sup>7</sup>

## RESULTS AND DISCUSSION

The dominant metal containing ions for the complex are shown in Fig. 1. The proposed probable formula is suggested on the basis of the various fragmentation patterns of the compound studied and the previously established fragmentation processes for the Schiff base metal complexes<sup>4-7</sup>. The m/e values are calculated for the most abundant isotope of the element present. In the effort to clarify the fragmentation process, a survey of the mass spectra for metastable ions is carried out.

Germanium occurs in several isotopic forms and out of these three having masses 74, 72 and 70 are important. However, the first isotope is the most abundant (37.1%). In the mass spectrum, a particular ion consisting of germanium shows the expected combination of peaks corresponding to the various isotopes of germanium. The molecular ion peak is observed at m/e 528 and two other peaks corresponding