

$$K = (A_0/P) + (g_0 - 2.0023). \quad (6)$$

The magnetic moment of the complexes (table 2) clearly indicate the absence of any anti-ferromagnetic coupling. The values further support that the complexes are mononuclear.

Conclusions:

1. The complexes under consideration are found to possess square planar $Cu[2N, 2O]$ moiety in chloroform.
2. In the solution of DMSO, DMF and pyridine, the coordination positions are found to be occupied by the solvent molecules.
3. The axial interaction of the solvent molecules is hindered if the size of the methylene bridge increases.
4. The bonding solvents pull the electron from copper.
5. The complexes are mononuclear in these solvents and the anti-ferromagnetic coupling is absent.

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COORDINATION-POLYMERS OF Mn(II), Co(II), Ni(II), Cu(II) AND Zn(II) WITH SOME NOVEL SCHIFF BASES

D. K. DWIVEDI

Chemical Laboratories, Atarra College, Atarra 210 201, India.

THE demand for new polymeric materials with high thermal and chemical stability has stimulated research in polymer chemistry¹⁻⁸. The present study is concerned with the preparation and characteri-

zation of coordination polymers of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) with the Schiff bases derived from 2-hydroxy-1-naphthaldehyde with *o*-dianisidine (DNDA), *p*-phenylenediamine (DNPPA), and benzidine (DNBN). The complexes were characterized by analytical, magnetic, thermogravimetric and spectral data.

Preparation of the Schiff-bases

The diamine (dianisidine or paraphenylenediamine or benzidine) solution in acetone (50 c.c. of 0.01 M) was added dropwise to 0.02 mol solution of 2-hydroxy-1-naphthaldehyde in 50 c.c. acetone with continuous stirring. The mixture was heated for about 30 min on a water bath and allowed to cool overnight. The resulting coloured precipitates were filtered, repeatedly washed with hot acetone and dried under suction. The purity of the compounds was checked by TLC, yield 60–70%.

The schiff bases are insoluble in water, ethanol, chloroform and acetone but soluble in DMF. The composition is given in table 1.

The schiff bases of 2-hydroxy-1-naphthaldehyde with *o*-dianisidine, paraphenylene diamine and benzidine are abbreviated as DNDA(L), DNPPA-(L') and DNBN(L'') respectively.

A mixture of 0.002 mol solution of schiff base (DNDA/DNPPA/DNBN) in hot DMF and 0.002 mol solution of the metal salt in DMF-H₂O, was refluxed over sand bath for 3 to 6 h. The coloured precipitates were filtered, washed with hot DMF and dried. All the complexes were coloured, stable, insoluble in common organic solvents (ethanol, acetone, carbon tetrachloride, methanol, benzene, *n*-hexane, DMF and DMSO).

The analytical data of the complexes (table 1) agree with the general formula $(ML_2 \cdot 2H_2O)_n$ where M = Mn(II), Co(II), Ni(II), Cu(II) or Zn(II) and L = L or L' or L''. However in the case of Cu(II)-DNPPA and Cu(II) DNBN, there are two additional molecules of associated H₂O. Zn(II) complexes with L' and L'' could not be isolated. The analytical values of the ligand and the metal complexes for C, H and N agreed with the calculated values within 1.4%. The colour and composition of the complexes are given in table 1.

The spectra of the compounds show characteristic band near 3400 in DNDA, DNBN and at 3300 in DNPPA; 1315 DNDA, DNBN and DNPPA are attributed to O–H stretching and deformation respectively. The absorptions near 1555–1530 and 1290–1265 may be assigned to C–O stretching and

Table 1 Colour and analytical data of the complexes

Compound	Colour	Elemental metal. found/calc.	Decomposition Temp (°C)
H ₂ L	Deep-red	—	(275° M.P.) (uncorrected)
(MnL.2H ₂ O) _n	Reddish-brown	8.02/8.58	340
(CoL.2H ₂ O) _n	Reddish-brown	9.10/9.16	300
(NiL.2H ₂ O) _n	Red	9.03/9.14	300
(CuL.2H ₂ O) _n	Reddish-brown	9.82/9.70	300
(ZnL.2H ₂ O) _n	Yellowish-brown	9.92/9.98	380
H ₂ L'	Red	—	(310° M.P.) (uncorrected)
(MnL'.2H ₂ O) _n	Brown	10.05/10.89	340
(CoL'.2H ₂ O) _n	Reddish-brown	11.43/11.59	280
(NiL'.2H ₂ O) _n	Red	11.68/11.57	300
(CuL'.2H ₂ O) _n .2H ₂ O	Brown	11.01/11.47	300
H ₂ L''	Yellowish-red	—	(305° M.P.) (uncorrected)
(MnL''.2H ₂ O) _n	Reddish-brown	8.98/9.47	380
(CoL''.2H ₂ O) _n	Orange-red	10.40/10.09	320
(NiL''.2H ₂ O) _n	Red	10.32/10.07	320
(CuL''.2H ₂ O) _n .2H ₂ O	Yellowish-brown	10.52/10.08	300

H₂L = DNDA = C₃₆H₂₈N₂O₄; H₂L' = DNPPA = C₂₈H₂₀N₂O₂; H₂L'' = DNBN = C₃₄H₂₄N₂O₂.

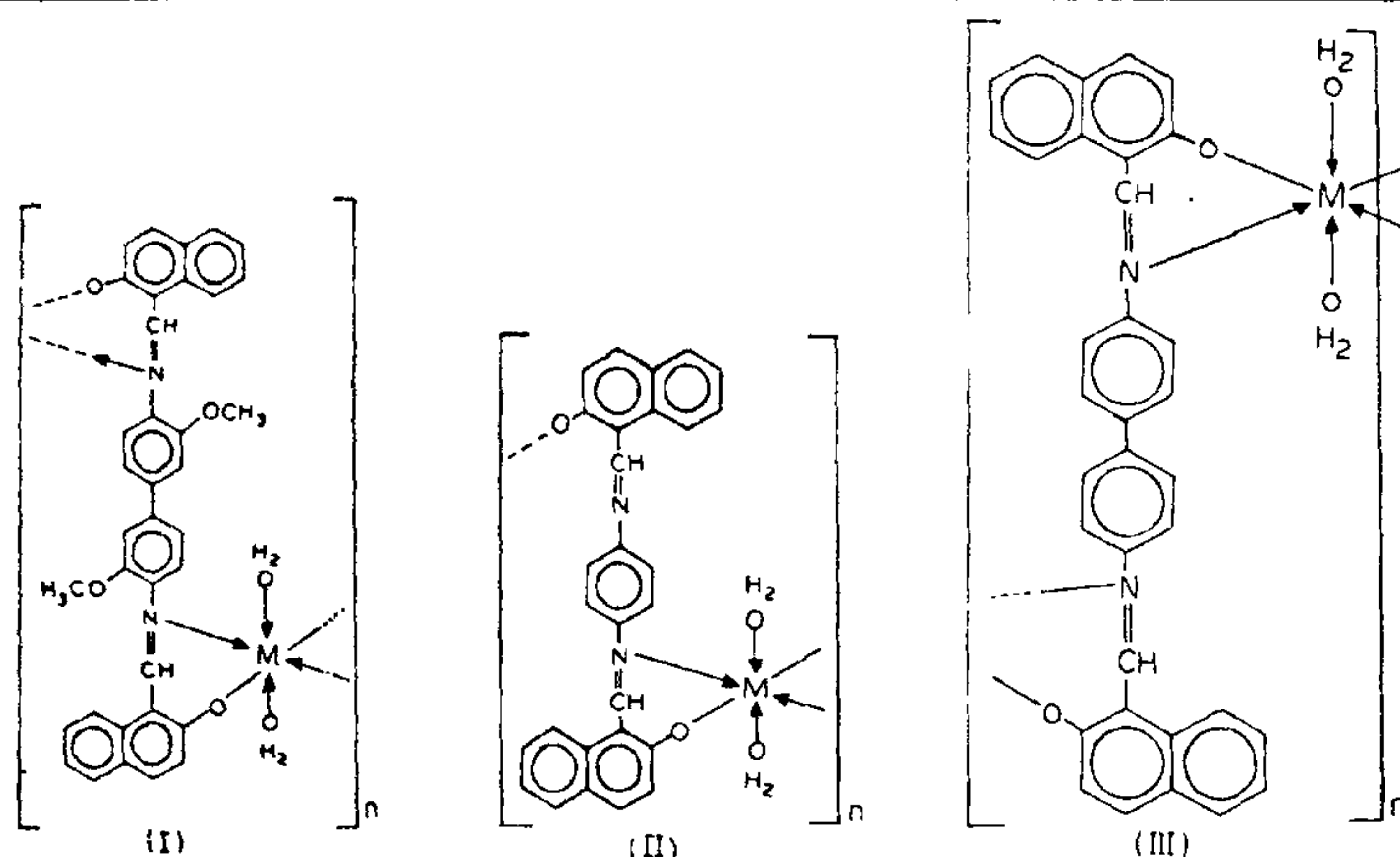
C—O deformation respectively due to phenolic group. The formation of schiff bases is indicated by the appearance of C=N stretching bands in the region 1655–1625. The disappearance of O—H stretching and O—H deformation bands in the complexes suggests the involvement of phenolic-

OH in complexation. This is further confirmed by positive shift of 3–10 in C—O stretching and C—O deformation frequency. The involvement of azomethine nitrogen in complexation is indicated by the negative shift of C=N stretching by 15–65 in the complexes. Association of water molecules in the

Table 2 Magnetic moment, electronic spectral data and ligand field parameters of complexes

Complex	H ₂ L (cm ⁻¹)	H ₂ L' (cm ⁻¹)	H ₂ L'' (cm ⁻¹)	Assignment	Magnetic moment (BM)	ν_2/ν_1	10Dq	B'	β	β° (%)
Mn(II)	19418	19230	18518	6A _{1g} → 4T _{1g} (G)	5.89 ^I	—	—	—	—	—
	23256	21505	20833	→ 4T _{2g} (G)	5.96 ^{II}	—	—	—	—	—
	24390	22727	21739	→ 4E _g (G)	5.91 ^{III}	—	—	—	—	—
	29412	26316	24272	→ 4T _{2g} (D)	—	—	—	—	—	—
	31250	28571	28581	→ 4E _g (D)	—	—	—	—	—	—
Co(II)	10810	10000	10152	4T _{1g} → 4T _{2g} (F)	4.85 ^I	2.11 ^I	12100 ^I	951 ^I	.988 ^I	1.20 ^I
	22910	21263	21582	→ 4A _{2g} (F)	4.57 ^{II}	2.12 ^{II}	11263 ^{II}	851 ^{II}	.876 ^{II}	12.30 ^{II}
	23810	21505	21739	→ 4T _{1g} (P)	4.92 ^{III}	2.12 ^{III}	11430 ^{III}	857 ^{III}	.883 ^{III}	11.74 ^{III}
Ni(II)	10869	10638	10000	3A _{2g} → 3T _{2g} (F)	3.09 ^I	1.63 ^I	10869 ^I	963 ^I	.912 ^I	8.80 ^I
	17544	17077	15626	→ 3T _{1g} (F)	3.10 ^{II}	1.62 ^{II}	10638 ^{II}	925 ^{II}	.876 ^{II}	12.32 ^{II}
	29412	28571	25000	→ 3T _{1g} (P)	3.02 ^{III}	1.57 ^{III}	10000 ^{III}	715 ^{III}	.677 ^{III}	32.29 ^{III}
Cu(II)	10205	11111	10205	2B _{1g} → 2A _{1g}	1.95 ^I	—	12263 ^I	—	—	—
	13793	13158	14285	→ 2B _{2g}	1.96 ^{II}	—	12198 ^{II}	—	—	—
	16260	16667	16129	→ 2E _g	2.10 ^{III}	—	12255 ^{III}	—	—	—

I = H₂L, II = H₂L', III = H₂L''.



Figures I-III.

complexes is confirmed by the appearance of new bands in the region 3600–3300, 1670–1600 and 970–900 assigned to O–H stretching, O–H deformation and rocking mode of coordinated water. The Cu(II) complexes with L' and L'' show weight losses at 160–150° equal to 6.55% and 5.83% respectively. These weight losses correspond to two lattice water molecules. The remaining two molecules of coordinated water are lost between 160 and 225°. The weight losses in the remaining polychelates at 180–310° are equivalent to two coordinated water molecules per repeating unit of polychelates. Thus coordinated water is lost between 180 and 310° and the lattice water between 100 and 160°. The additional two molecules of water in Cu(II) of L', L'' are also supported by elemental analysis. Non-ligand bands due to M–N and M–O vibrations are observed in the region 585–520 and 490–410 respectively⁹⁻¹¹.

Mn(II), Co(II), Ni(II) and Cu(II) complexes are paramagnetic while Zn(II) DNDA is diamagnetic, various ligand field parameters, viz., ν_2/ν_1 , $10Dq$, B' , β , β^0 have been calculated¹² (table 2) from electronic spectral data. Magnetic moments have also been measured. Both these data show octahedral geometry of the complexes. The order of thermal stability for DNDA complexes is as follows:

Zn(II) > Mn(II) > Co(II) \approx Ni(II) \approx Cu(II) for DNPPA complexes

Mn(II) > Ni(II) \approx Cu(II) > Co(II) and for DNBN complexes

Mn(II) > Ni(II) \approx Co(II) > Cu(II).

For Cu(II) complexes g values are found to be < 2.3 which suggest that they are covalent in nature.

The nature of ligand, composition (M:L::I:I) insolubility and high thermal stability (280–380°) of the complexes indicate their polymeric nature^{1-3, 6-8, 13-16}. The tentative structures are suggested in figures I, II, III.

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HISTOCHEMICAL DISTRIBUTION OF ACID PHOSPHATASE AND ALKALINE PHOSPHATASE ACTIVITIES IN THE CEREBRAL GANGLION OF THE CRAB *POTAMON MAGNUM MAGNUM* (PRETZMAN)

L. J. RASHAN

Department of Biology, College of Education,
University of Mosul, Mosul, Iraq.

This report is a continuation of our efforts to describe the histochemical nature of the thoracic and cerebral

neurosecretory cells of the crab, *Potamon magnum magnum*¹.

Very little is known about the enzyme histochemistry of the crustacean nervous system. The present investigation was undertaken to demonstrate the distribution of acid and alkaline phosphatases in the cerebral ganglion of *P. m. magnum*.

Adult crabs were collected during February 1982 from the suburbs of Mosul city. Paraffin sections 8 μ m thick were obtained after fixing the ganglia in cold acetone at 4°C. Gomori's techniques for acid and alkaline phosphatases were followed².

In the alkaline phosphatase preparation, the neural sheath displays a moderate reaction. However, the nuclear membrane, nucleolus and the secretory granules are also stained brownish-black indicating the presence of some enzyme activity (figure 1). The neurosecretory granules are few and they are dispersed throughout the cytoplasm of the cells and in the axons. On the other hand, in the acid phosphatase preparation, the intensity of colour is very weak. All cell components including the secretory material in both types of cell react in the same way (table 1). Nevertheless, the neural sheath exhibits a little stronger reaction in comparison with the cell components. Again, the neurosecretory granules are scarce.

Investigations on the distribution of alkaline phosphatase in both vertebrate and the invertebrate nervous systems have shown that this enzyme displays a peripheral distribution near the cell surface³⁻⁷

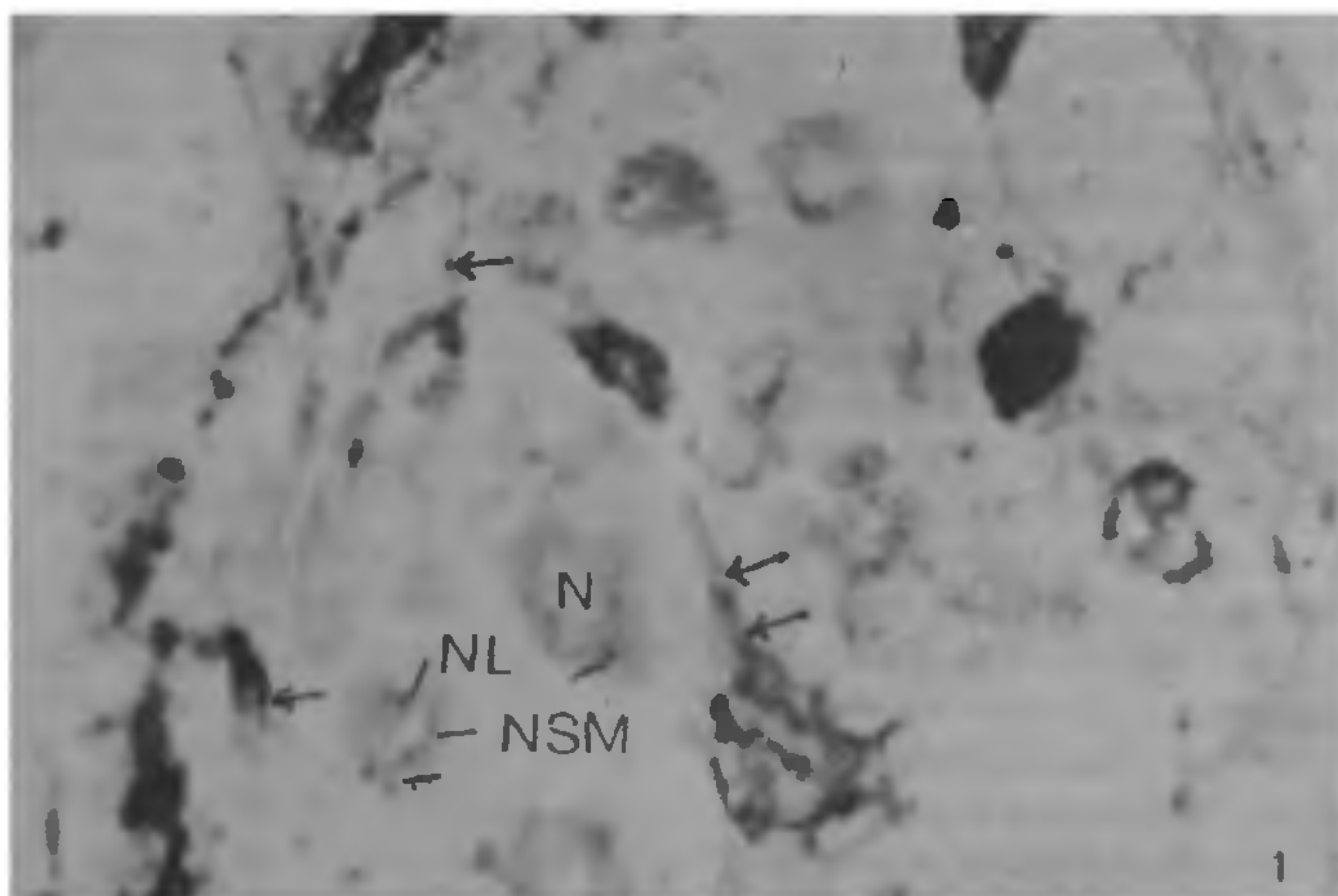


Figure 1. Horizontal section through the cerebral ganglion of *Potamon magnum magnum* showing neurosecretory cells. [NSM, neurosecretory material; N, nucleus; NL, nucleolus]. Arrows indicate moderate alkaline phosphatase reaction in the neural sheath. Calcium-cobalt method ($\times 800$).