

# Communications

## New Binuclear Nickel(II) Species

B. S. RAGHAVENDRA, R. H. BALUNDGI & A. CHAKRAVORTY  
Department of Chemistry, Indian Institute of Technology  
Kanpur 208016

Received 19 August 1976

By reacting trimeric bis(acetylacetonato)nickel(II) with some tridentate Schiff base ligands, new dinuclear mixed ligand species have been obtained. A probable structural model for such species is proposed.

**T**RIMERIC bis(acetylacetonato)nickel(II),  $Ni_3(acac)_6$  has fused octahedral  $NiO_6$  coordination spheres<sup>1</sup>. The dinuclear fragment  $Ni_2(acac)_4$  is coordinatively unsaturated and yields adducts<sup>2</sup> such as  $Ni_2(acac)_4(pyridine)$  in which the nickel(II) is again octahedral. One may expect that species of type  $Ni_2(acac)_3T$  (T = tridentate monoanionic ligand) with octahedral nickel(II) should exist. It has indeed been possible to isolate such species using the tridentate ligand  $Hsal nR_2$  (Ia).

The Schiff base (Ia) was prepared by heating to reflux (0.5 hr) salicylaldehyde and the amine in equimolar proportions in ethanol. The solvent was removed on a rotary evaporator. The Schiff base (0.1 mole) and  $Ni_3(acac)_6$  (0.07 mole) were taken in 75 ml toluene. The reaction mixture was heated

to reflux for 1 hr. The green solution was then filtered and cooled. Hexane was added to initiate crystallization where needed. The green complex was obtained in 50% yield. (Even when twice the above amount of Schiff base was used in the preparation the product isolated remained the same.) Analytical and molecular weight data (Table 1) establish the composition  $Ni_2(acac)_3(saltnR_2)$ .

All the complexes show an IR band (Table 2) in the region 1620-1630  $cm^{-1}$  assigned to  $\nu C=N$  of the Schiff base moiety. There are two strong bands at  $\sim 1590$  and  $\sim 1510$   $cm^{-1}$  which are due to the combination of  $\nu C=C$  and  $\nu C=O$  of  $acac^3$  with additional contributions from aromatic vibrations of the Schiff base. The complexes are fully paramagnetic (Table 2). Their ligand field spectra (Table 2) are closely akin to that<sup>4</sup> of  $Ni_3(acac)_6$ . On the basis of model-building it is proposed that the  $Ni_2(acac)_3(saltnR_2)$  has the structure (II) in which only  $acac$  occupy bridging position.

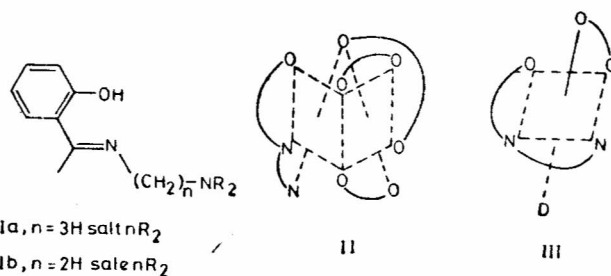


TABLE 1 --- CHARACTERIZATION AND MOLECULAR WEIGHT DATA

Compound	m.p. (°C)	Calc. (%) (Found)				Mol. wt. <sup>(a)</sup>	
		C	H	N	Ni	Calc.	Found
$Ni_2(acac)_3(saltnMe_2)$	201	52.30 (52.28)	6.18 (6.08)	4.52 (4.17)	18.93 (18.97)	620	565
$Ni_2(acac)_3(saltnEt_2)$	151	53.75 (54.25)	6.53 (6.50)	4.32 (4.41)	18.12 (18.31)	—	—
$Ni_2(acac)_3(saltnBu_2)$	160	56.28 (56.30)	7.15 (6.96)	3.97 (4.06)	16.67 (16.58)	704	675

(a) Molecular weights were determined cryoscopically in purified dry benzene.

TABLE 2 — PHYSICAL DATA<sup>(a)</sup>

Compound	IR bands ( $cm^{-1}$ ) <sup>(b)</sup>		Magnetic moment per Ni(BM) <sup>(c)</sup>		Electronic spectra in benzene <sup>(d)</sup>
	$\nu C=N$	$\nu C=O + \nu C=C$ + aromatic	Solid	Solution (chloroform)	
$Ni_2(acac)_3(saltnMe_2)$	1623	1591; 1508	3.22	3.21	8550 (9); 15750 (11)
$Ni_2(acac)_3(saltnEt_2)$	1627	1591; 1509	3.22	3.20	8550 (10); 15750 (14)
$Ni_2(acac)_3(saltnBu_2)$	1628	1593; 1508	3.24	3.26	8550 (10); 15385 (13)

(a) All the data given in the table were recorded at room temperature (25-27°C).

(b) IR spectra were recorded on a Perkin-Elmer 521 recording spectrophotometer.

(c) Magnetic moments were measured using a sensitive Gouy balance.

(d) Electronic spectra were recorded on a Cary model-14 recording spectrophotometer. Band positions are in  $cm^{-1}$ ; extinction coefficients per Ni (given in parentheses) are in  $litre\ mol^{-1}\ cm^{-1}$ .

We note that the reaction of  $Ni_2(acac)_6$  with ligand (Ib) yields mononuclear pentacoordinated  $Ni(acac)(salenR_2)$  which readily forms octahedral adducts (III) with monodentate donors<sup>5</sup>. No evidence for dinuclear species has been obtained with this ligand. The difference in the behaviour of Ia and Ib can be rationalized on the basis of structure (II). In this structure the  $salenR_2$  ligand occupies three facial positions of an octahedron. The flexible  $-(CH_2)_3-$  chain makes this possible<sup>6</sup>. On the other hand  $salenR_2$  can only span meridional positions<sup>7</sup> (as in III) due to relative shortness of the  $-(CH_2)_2-$  chain. It cannot span facially.

Financial assistance given by Department of Atomic Energy, Government of India, is gratefully acknowledged.

#### References

1. BULLEN, G. J., MASON, R. & PAULING, P., *Inorg. Chem.*, **4** (1965), 456.
2. GRADON, D. P., *Coord. Chem. Rev.*, **4** (1969), 1.
3. NAKAMOTO, K., *Infrared spectra of inorganic and coordination compounds* (Wiley-Interscience, New York), 1970, 247.
4. JORGENSEN, C. K., *Acta Chem. scand.*, **9** (1955), 1362.
5. BALUNDGI, R. H. & CHAKRAVORTY, A., *Inorg. Chim. Acta*, **8** (1974), 261.
6. DI VAIRA, M. & ORIOLI, P. L., *Inorg. Chem.*, **5** (1967), 490.
7. SACCONI, L., ORIOLI, P. L. & DI VAIRA, M., *J. Am. chem. Soc.*, **87** (1965), 2059; ORIOLI, P. L., DI VAIRA, M. & SACCONI, L., *J. Am. chem. Soc.*, **88** (1966), 4383; TEWARI, R., SRIVASTAVA, R. C., BALUNDGI, R. H. & CHAKRAVORTY, A., *Inorg. nucl. Chem. Lett.*, **9** (1973), 583.

### Chemical Oscillations in $Mn^{2+}$ -catalysed Belousov-Zhabotinskii Reaction in Orthophosphoric Acid Medium

K. PRASAD\*, G. S. P. VERMA, A. PRASAD & V. B. DHAR

Department of Chemistry, Ranchi University, Ranchi 834008

Received 22 April 1976; accepted 19 June 1976

The occurrence of Belousov-Zhabotinskii reaction in orthophosphoric acid medium is reported for the first time. The existence of two alternate mechanisms for the observed chemical oscillations in this system is suggested.

OSCILLATORY reaction between potassium bromate, malonic acid, and cerous/ceric ion in sulphuric acid medium has received considerable attention<sup>1-6</sup>. In this reaction malonic acid may be replaced by a number of organic substances containing active methylene group which can be easily brominated by enol mechanism<sup>7</sup>. The catalyst, the

cerous/ceric ion, can also be replaced by a number of metal ions capable of existing in two valence states differing by one electron only and having their  $E_0$  values between 0.9 and 1.6 (ref. 7). However, no alternative to sulphuric acid medium for this reaction has, as yet, been reported. In this paper we report our observations on chemical oscillations in orthophosphoric acid medium. The work is all the more significant in view of chemical oscillations found in biological systems containing enough of phosphate group.

Potassium bromate (Baker analysed), manganous sulphate (S. Merck/GR), malonic acid (Riedel, extrapure) and orthophosphoric acid (E. Merck/GR) were used as such.

**Procedure**—The reaction was followed potentiometrically using bright Pt wire as indicator electrode and SCE as reference. Potassium chloride was found to inhibit oscillations and so a very dilute solution of KCl (0.002M) was taken in the calomel electrode. The two half cells were connected with the help of potassium sulphate agar agar bridge. The e.m.f. of the system was determined using direct reading potentiometer (Titricomat, ILM LABOR, GDR). To a solution containing orthophosphoric acid, malonic acid and manganous sulphate equilibrated at  $35^\circ \pm 0.1^\circ$ , was added a solution of potassium bromate also equilibrated at this temperature. The bright Pt indicator electrode was inserted in the vessel and e.m.f. recorded at varying time intervals. The results are plotted in Fig. 1.

The oscillation in the present system is found to be qualitatively different from that found in sulphuric acid medium. The total oscillatory state of the system can be divided into three parts (Fig. 1). The oscillatory states from A to B and from C to D are similar to that found in Belousov-Zhabotinskii reaction system in sulphuric acid medium. These states are characterized by a slight increase in time period with time.

The state from B to C is unique. It shows alternate long and short periods,  $L_1, S_1; L_2, S_2; \dots$ .  $L_i, S_i$ , suggesting that the system has two alternate cyclic routes by which it reaches the autocatalytic state signalled by a sudden rise of e.m.f. of the system. The shorter time period is associated with shorter amplitude whereas the longer time period is associated with longer amplitude. These amplitudes can be related to the difference between the upper and lower critical [bromide ion] limits<sup>8,9</sup>. Thus it seems that the two alternative routes are having two pairs of critical [bromide ion] limits under two different conditions. More work is required to elucidate this point.

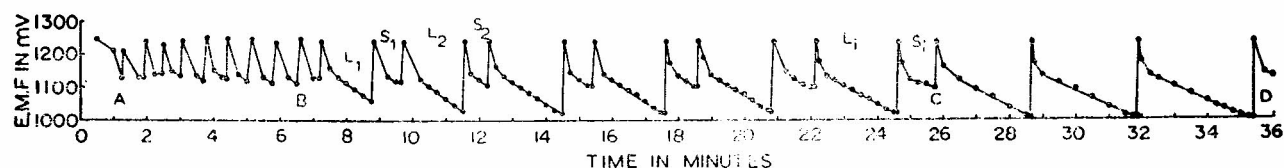


Fig. 1—Plot of e.m.f. against time at  $35^\circ$  ( $[Malonic\ acid] = 0.032M$ ,  $[KBrO_3] = 0.044M$ ,  $[MnSO_4] = 0.0008M$  and  $[H_3PO_4] = 8.4N$ )

\*To whom correspondence regarding the paper may be made.