integrated for fifteen protons and showed the following signals: 2.4 (s, 6H, Ar-CH₃), 4.3 (b, s, 2H, NH₂), $7.0 \sim 8.0$ (m, 7H, aromatic).

From the above evidence the compound was assigned the structure (IIa). The latter is consistent with the observation that on boiling it with either acetic anhydride or with dilute hydrochloric acid the original compound (Ia) was obtained in almost quantitative yield.

The formation of IIa may be due to the opening of the coumarin ring in (Ia) by a strong base like hydraline hydrate giving the hydroxy hydrazide as an intermediate which recyclizes to give back the resulting compound.

The reaction also succeeds with other 4H-1-benzopyrano (3, 4-d) oxazole-4-one derivatives. The compound (IIb) had m.p. 158-60°. However, a similar hydrazide formation is not observed with 4H-1-benzothiopyrano (3, 4-d) oxazol-4-ones.

The same reaction occurs also in the case of the known³ 3-methyl- and 3-ethyl-4H-1-benzopyrano (3, 4-d)-isooxazol-4-ones giving the corresponding hydrazones IVa, m.p. 148-50°, IVb, m.p. 114-16°.

In our procedure for the preparation of the two isnowazol-4-ones, which is somewhat different from that reported,3 the oximes of 4-hydroxy-acetyl- and 4-hydroxy-3-propionyl coumarins were acetylated to yield the corresponding unknown acetates of the oximes, m.p. 183-84° and 128-30° respectively. The oxime acetates on boiling with pyridine afforded the required isooxazole-4-ones in 50-60% yields.

With a view to study the general applicability of the reaction we studied the reaction of hydrazine hydrate with 7-hydroxy-3-ethyl-4-methylcoumatin. In this case the reaction failed and the original coumarin was obtained back. The reaction was unsuccessful with 7-hydroxy-6-ethyl-3, 4-cyclopenteno- and 7-hydroxy-6-ethyl-3, 4-cyclohexenocoumatins. The reactions also failed to give a pure product with 4-methoxy-6-methylcoumatin. It, therefore, seems that the presence of an oxazole or an isooxazole ring in 3, 4 positions is very necessary for the reaction to occur.

All compounds gave satisfactory C, H and N analyses.

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- 1. Merchant, J. R. and Shirali, S. S., Chem. and Ind., 1977, 1, 33.
- 2. Baddar, F. G., Al-Hajjar, F. H. and El-Rayyes, N. R., J. Het. Chem., 1976, 13, 195.
- 3. Desai, M. K. and Usgaonkar, R. N., Indian J. Chem., 1977, 4, 379.

AMINOPHOSPHINE COMPLEXES OF COPPER(II), COBALT(II) AND NICKEL(II)

COMPOUNDS, in which tervalent phosphorus being bound to the nitrogen directly and also forming co-ordinate bonds with metals, have been little investigated so far. These amino-phosphines clearly serve as potential ligands for many metal ions¹⁻⁶. The present paper records the synthesis and characterisation of some aminophosphine complexes of copper(II), cobalt(II) and nickel(II) phthalimides.

The aminophosphine used in the study is diphenyl-pyridylphosphine (A) and has been obtained by the treatment of diphenylchlorophosphine with pyridinse in anhydrous ether, followed by crystallisation. When treated with copper(II), cobalt(II) and nickel(II) phthalimides, it yields blue and pink coloured complexes, the structures of which have been resolved on the basis of elemental analysis, conductivity, magnetic susceptibility and electronic spectra.

(i) Diphthalimido (diphenylpyridylphosphine)
Copper(II)

Found C = 67.90%; H = 3.25%; N = 6.95%. Calcd. C = 67.35%, H = 3.90%; N = 7.10%

(ii) Diphthalimidobis (diphenylpyridylphosphina) Cobalt (II).

Found C = 73.62%; H = 4.90%; N = 7.20%. Calcd. C = 73.44%; H = 4.65%; N = 6.98%.

(iii) Diphthalimidobis (diphenylpyridylphosphina) nickel(II).

Found C = 74.00%; H = 4.92%; N = 7.54%. Calcd. C = 73.49%; H = 4.70%; N = 7.02%.

The conductivity of the complexes was measured in nitrobenzene on a Philips PR 9500/90 magic eye type instrument. Magnetic susceptibility was obtained by Gouy's method, at room temperature while the electronic spectra were measured in the form of solid samples on a Cary 14 recording instrument.

The molar conductances of the complexes are in the range 0.5-0.75 mhos in nitrobenzene and indicate the neutral nature of the complexes. It thus appears that the two phthalimide (phth) ions besides neutralising the charge of the metals are also coordinated to it, and the formulas of the complexes can be represented as [Cu(phth),A], and [Co or Ni(phth),A]

which indicate that the aminophosphine is acting as a bidentate ligand, since both nitrogen and phosphorus atoms contain lone pair of electrons. Tetra- and hexa-coordinated complexes are formed in the case of copper(II), cobalt(II), and nickel(II) respectively-

Copper(II) complex: The $\mu_{\rm eif}$ value of the complex is 1.90 B.M. characteristic of square planar structure. In confirmation of this structure, only one band is seen in the entire visible region at 680 nm? corresponding to the D_{α} value of 146 cm⁻¹.

Cobalt (II) complex: The complex possesses high spin obtahedral structure as shown by (i) its μ_{i} value which is 4.60 B.M. and (ii) the presence of ν_{3} and ν_{1} transitions at 20.00 kK and 9.99 kK respectively. The ν_{2} band is not clearly visible in the spectrum. The D_{q} and B values for the complex are calculated to be 844.0 and 879.2 cm⁻¹.

Nickel(II) complex: This dark pink complex gives a μ_{il} value of 3.80 B.M. suggesting the octahedral disposition of ligands around the metal. As seen in case of other octahedral complexes of the metal, three bands are observed in the spectrum at 8.9, 14.5 and 27.3 kK which have been assigned to be ν_1 , ν_2 and ν_3 transitions. The values for the two ligand field parameters, i.e., D & B are 900.1 and 905 cm⁻¹ respectively.

These compounds belong to the class of mixed ligard complexes, as different ligands are coordinated to the metal and the D, values indicate that the ligand fields around the metal ion is quite strong?. The Racah parameter B is reduced to some 80-90% of the free ion value for the cobalt(II) and nickel(II) complexes respectively, suggesting a considerable degree of covalency in the complexes.

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1. Michaelis. Annalen, 1903, 326, 179.

OCCURRENCE OF SEISMITE IN THE PRECAMBRIAN ROCKS OF RAJASTHAN, INDIA Observations:

The semipelites of the Aravalli Supergroup (Precambrian) exposed in the Anas river show intraformational micro-faults, 2.5 Km test of Chandanwara Fort (Lar N 23° 27', Long. E 74° 06' 30") Banswara District, Rajasthan, India. Intraformational faulting was observed in a zone of 25 cm over a strike length of one metre. In strike continuity seismite grades to wave disturbed rocks.

Soupy Zone and Segmented Zone of the fault graded seismites described by Seilacher¹ are recognisable in outcrop, as described in Plate I.



FLATE I. Section along strike of seismite bed and perpendicular to bedding (Pencil for scale, 12 cm). a-Soupy Zone, b-Segmented Zone, c-Undisturbed Sediments.

Soupy Zone: It is characterised by indistinct lamination near the base and structureless admixture of quartz and sheet minerals towards the top. In the proximity of the faults of 10 cm to 15 cm vertical length flocculation has obliterated earlier depositional structures.

Segmented Zone: It represents coherent layers at the sediment water interface and slightly below. The zone is characterised by micro-faults which extend vertically from 2 mm to 15 cm, showing vertical displacement of 1 mm to 5 mm and occur as step faults. In some of the layers, the faults cut both top and bottom of the beds, but in a few layers these are confined to the bottom, the top surface of the bed remain unaffected. The step faults are both normal and reverse type. In both normal and reverse faults, the fault planes dip towards southwest.

Undisturbed Sediment: This zone represents undeformed laminations and a sort of micro-uncon-

^{2.} Harris, G., S., J., Chem. Soc., 1958, Part 1, 512.

^{3.} Anton, B Burg and Peter I. Slota, Jr., J. Am. Chem. Soc., 1958. 80, 1107.

^{4.} Kurt Issleib and Wolfgang Seidel, Chem. Ber., 1959, 92 (2), 2681.

^{5.} Harry, H. Sister and Nathan, L. Smith, J. Org. Chem., 1961, 26, Pt. 1, 611.

^{6.} Ewart, G., Payne, D. S., Porte, A. L. and in 1977. Lane, A. P., J. Chem. Soc., 1962, Pt. 3. 3984.

^{7.} Finnis. R N.. Introduction to Lineard Folls' Wiles Fastern Ltd., New Delhi, 1966, pp. 221

^{78&#}x27;. Madan, S. K. and Mueller, D., J. Inorg. Nucl. Chem., 1966, 28, 177.