

* Present address : Vice-Chancellor, Sri Venkateswara University, Tirupati, Andhra Pradesh.

1. Brandrup, J. and Immergut, B. H., *Polymer Handbook*, 1966, 4.
2. Yoshinobu Isumi and Yasuhiro Miyake, *Polymer J.*, 1973, 4, 205.
3. Berry, G. C., *J. Chem. Phys.*, 1967, 46, 1338.
4. Kurata, M. and Stockmayer, W. H., *Fortschr. Hochpolymer. Forsch.*, 1963, 3, 196.
5. Kuwahara, N., Ogino, K., Kasai, A., Veno, S. and Kaneko, M., *J. Polymer. Sci., Part A*, 1965, 3, 985.
6. Takamizawa, K., *Bull. Chem. Soc., Japan*, 1966, 39, 1186.
7. Saito, T., *Ibid.*, 1962, 35, 1580.
8. Mohitie, R. S., Gundiah, S. and Kapur, S. L., *Makromol. Chem.*, 1968, 116, 280.
9. Noguchi, Y., Aoki, A., Tanaka, G. and Yamakawa, H., *J. Chem. Phys.*, 1970, 52, 2651.
10. Matsumura, K., Fukaya, M. and Mizuno, K., *Bull. Chem. Soc., Japan*, 1970, 43, 1881.
11. Fox, T. G. and Flory, P. J., *J. Am. Chem. Soc.*, 1951, 73, 1904.
12. Kurata, M., Stockmayer, W. H. and Roig, A., *J. Chem. Phys.*, 1950, 33, 151.
13. Stockmayer, W. H. and Fixman, M., *J. Polymer. Sci.*, 1953, C1, 137.
14. Inagaki, H., Sazuki, H. and Kurata, M., *Ibid.*, 1966, C15, 409.
15. Bohdanecky, M., *Ibid.*, 1965, B3, 201.
16. Cowie, J. M. G., *Polymer*, 1966, 7, 487.
17. Berry, G. C., *J. Chem. Phys.*, 1967, 46, 1338.
18. Veda, M. and Kajitoni, K., *Makromol. Chem.*, 1967, 108, 138.
19. Huggins, M. L., *J. Am. Chem. Soc.*, 1942, 64, 2716.
20. Kraemer, E. O., *Ind. Eng. Chem.*, 1938, 30, 1200.
21. Flory, P. J., *Principles of Polymer Chemistry*, Cornell Univ. Press, Ithaca, New York, 1953, Chapter 14.
22. Jenkins (Ed.), A. D., *Progress in Polymer Science*, Pergamon Press, Oxford, 1967, Vol. 1, Ch. 1.

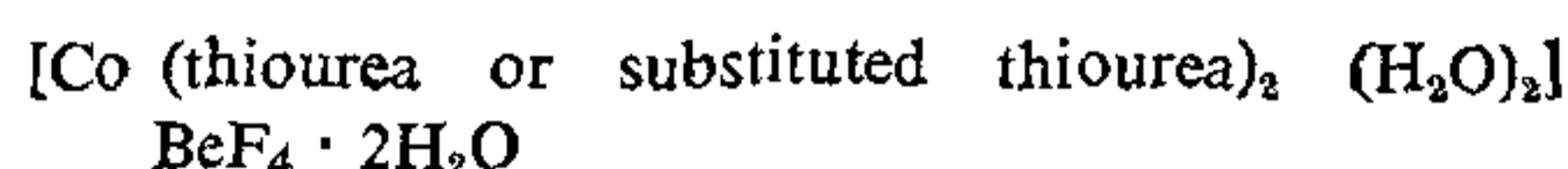
SYNTHESIS AND SPECTRAL CHARACTERISTICS OF SOME MIXED LIGAND Co(II) COMPLEXES

Introduction

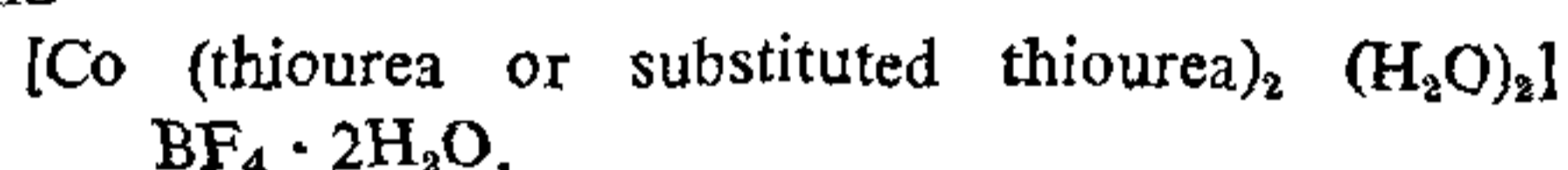
THE study of electronic absorption spectra has been found useful in elucidating the ligand field theory to transition metal complexes¹⁻³. In the present paper the synthesis, spectral data and the computed values of some electronic spectral parameters of some mixed ligand Co(II) complexes of tetra fluoroberylate and tetrafluoroborate with thiourea and substituted thioureas have been given.

Experimental

The complexes have been synthesized by adding an ethanolic solution of thiourea (or substituted thiourea, viz., allyl thiourea phenylthiourea and diphenylthiourea) to an ethanolic solution of cobalt fluoroberylate (or Cobalt fluoroborate) in the molar ratio 2 : 1. The green crystals purified from water alcohol mixture were found to be soluble in ethanol, acetone and dimethyl formamide. The magnetic moment and spectral data suggest the following stoichiometry for the said complexes. The analytical data agree with the chemical composition as it has been suggested,



and



Physical Measurements

The magnetic moment measurements and electronic spectral measurements were recorded respectively on Gouy magnetic balance and Carl-Zeiss (VSU-2) spectro-photometer by using dimethylformamide solution of these complexes. The value of magnetic moment for these complexes is found to lie in between 4.90 to 5.29 B.M. (Bohr magneton).

Results and Discussion

There was a slight difficulty in locating the sharp peak positions of the three spin-allowed transitions in the electronic absorption spectra of these complexes. Probably, this was due to low intensity of ν_1 and ν_2 bands and a ligand absorption near UV region in case of ν_3 -band. Thus the numerical fitting methods² have been used to obtain the average value of B (a Racah parameter) and 10 Dq (Crystal field parameter).

Further, the computed values of B and 10 Dq by using above method have also been compared with the values obtained by using modified Tanabe-Sugano diagrams⁴. A close similarity in the values obtained by both the methods show an additional verification of the reported results. The spectral data and computed values of electronic spectral parameters are reported in Table I.

The values of β^0 show a trend of weak covalent bonding in these complexes whereas the values of the ratios ν_2/ν_1 and ν_3/ν_2 show an octahedral or near octahedral stereochemistry for these complexes. The values of other spectral parameters, viz., 10 Dq, B, C, D, F₂, F₄, F³, F⁴, β , β^0 , C.F.S.E., *h* and *f* the significance of which is given in the literature³⁻⁶ show a similar trend of spectral characteristics in these complexes.

Conclusions

In the present paper the emphasis is made on electronic spectral parameters to infer about bonding and

TABLE I
Spectral data and computed values of Spectral Parameters for some Co(II) complexes using their solutions in dimethylformamide.

Spectral data and parameters	Co(II) complexes of tetrafluoroberylate and tetrafluoroborate with thiourea and substituted thiourea							
	Cc(TF Be) (Tu)	Cc(TF Be) (AT)	Cc(TF Be) (PT)	Cc(TF Be) (DT)	Cc(TF Be) (Tu)	Cc(TF B) (AT)	Cc(TF B) (PT)	Cc(TF B) (DT)
1. Observed spin-allowed transitions in cm^{-1}	ν_1 8438.3 ν_2 16260 ν_3 19531	8510.6 16528 19618	8474.5 16260 19607	8474.5 16129 19417	8474.5 16393 19417	8438.8 16260 19607	8438.8 16260 19305	8403.3 16181 19230
2. Racah parameters ⁶ in cm^{-1} from numerical fitting methods.	B 789.1 C 3653 D 6565	788.1 3648 6557	796.3 3686 6625	781.8 3619 6504	776.0 3592 6456	799.6 3702 6652	740.1 3426 6157	775.8 3591 6454
3. Spin-pairing energy ⁶ in cm^{-1}	D	6557	6625	6504	6456	6652	6157	6454
4. C. F. S. E. ⁶ ($-8Dq$) in K. Cal/mole.	E	20.11	19.90	19.74	19.94	9.90	18.56	19.79
5. Slater-Condon ⁷ parameters in cm^{-1}	F_2 1307.6 F_4 104.37	1305.9 104.23	1319.5 105.31	1295.5 103.40	1285.9 102.63	1325.0 105.77	1226.4 97.89	1285.6 102.60
6. Slater-Condon shortley ⁸ parameters in cm^{-1}	F^2 43692 F^4 46027	43637 45964	44091 46443	43288 45593	42967 45259	44273 46645	40979 43167	42956 45246
7. Crystal field parameter in cm^{-1} from numerical fitting methods.	10Dq	8782	8691	8621	8709	8691	8104	8643
8. Crystal field and nephelauxetic parameters ⁶ for the ligand used in the complex.	f 0.94 h 0.79	0.94 0.79	0.93 0.75	0.93 0.79	0.94 0.83	0.93 0.75	0.87 1.00	0.93 0.83
9. Nephelauxetic ratio and percentage covalence character.	β 0.81 β^0 19.0	0.81 19.0	0.82 18.0	0.81 19.0	0.80 20.0	0.82 18.00	0.76 24.0	0.80 20.0
10. Ratios between ν_1 , ν_2 and ν_3 .	ν_3/ν_1 2.31 ν_3/ν_2 1.20	2.30 1.18	2.31 1.20	2.29 1.20	2.29 1.18	2.32 1.12	2.28 1.18	2.29 1.18
11. Average value of B and 10 Dq in cm^{-1} from modified Tanabe Sugano diagrams	B 845.6 10Dq (Graphical) 7629	843.5 8932	848.9 7658	840.7 8922	831.8 9005	842.8 8747	826.5 8987	823.5 8238

Where, TF Be = tetrafluoroberylate,
DT = diphenyl thiourea.

TF B = tetrafluoroborate, Tu = Thiourea, AT = allyl thiourea, PT = phenyl thiourea,

stereochemistry in some mixed ligand Co(II) complexes. The values of B and 10 Dq were determined by using modified Tanabe-Sugano diagrams. This elucidates an application of semi empirical ligand field theory to electronic absorption spectra of these complexes.

Authors are grateful to Prof. R. C. Kapoor and Prof. A. N. Nigam for their continued interest in the work.

Department of Chemistry,
University of Jodhpur,
Jodhpur,
April 23, 1979.

R. K. JAIN,
G. K. JOSHI,
SUDHINDRA N. MISRA.*

* For correspondence.

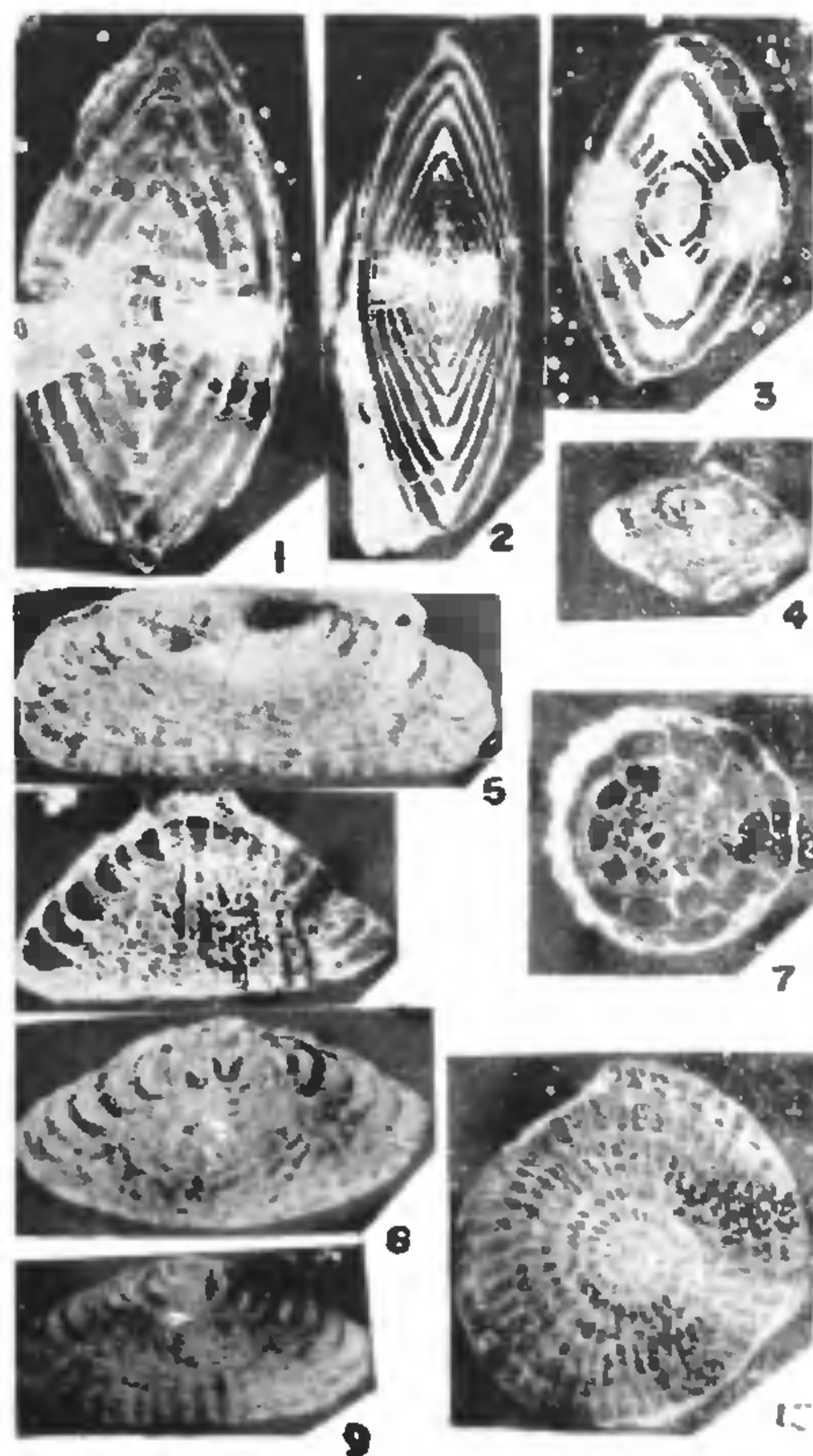
1. Rastogi, D. K. *et al.*, *J. Inorg. Nucl. Chem.*, 1975, 37, 685.
2. Konig, E., *Structure and Bonding*, 1971, 9, 175.
3. Jorgensen, C. K., *Absorption Spectra and Chemical Bonding in Complexes*, London, Pergamon Press, 1962.
4. Lever, A. B. P., *Advances in Chemistry Series*, 1966, 62, 435.
5. Allen, G. C. and Warren, K. D., *Structure and Bonding*, 1971, 9, 49.
6. Douglas, Bodie E. and Mc Daniel, Darl, H., *Concepts and Models of Inorganic Chemistry*, (Oxford and IBH Publishing Co., Calcutta, Bombay, New Delhi) Chapt. (X), 1970, p. 333.
7. Orgel, L. E., *J. Chem. Phys.*, 1955, 23, 1004.
8. Stanley Griffith, J., *J. Inorg. Nucl. Chem.*, 1956, 2, 1.

RANGE OF *DICTYOCONOIDES FLEMINGI*, DAVIES, 1937 AND THE AGE OF SUBATHU GROUP OF ROCKS OF INDIA

In the Palaeogene sequence of Lesser Himalayas, the rocks of Subathu Group have attracted much attention of the Indian micropalaeontologists. Geographically these beds are known to extend, in a narrow belt or isolated outcrops, from Jammu in the North-west to Nainital in the East. The corresponding rocks in the Tethys Himalaya are termed as Nummulitic beds as is generally used by various workers for *Nummulite* bearing rocks of other places.

Recently micropalaeontological investigations have been carried by Pant and Iqbaluddin¹⁻², Datta *et al.*,³⁻⁵ Srikantia and Bhargava⁶, Tewari and Kumar⁷, Tewari and Singh⁸, Mathur⁹, Srikantia and Sharma¹⁰, Singh¹¹⁻¹³, Chatterji and Pant¹⁴, Kumar¹⁵, Tewari and Prakash¹⁶, and Samanta¹⁷. The critical review of their work reveals that the presence of *Nomifomina* (?) sp., *Dictyoconoides flemingi*, *D. cf. flemingi*, *Dictyocathima dadahuensis*, *Lockhartia haimel*, *L. conditi*, *L. tipperi*, *Ranikothulia* sp. and *Assilina leymerei* are the main

foraminiferida on the basis of which Pant and Iqbaluddin¹⁻², Datta *et al.*,³⁻⁵ Srikantia and Bhargava⁶, and Mathur⁹, extended the lower age limit of Subathu Group of rocks to late Palaeocene. Samanta¹⁷ observed the absence of Palaeocene foraminiferal fauna in Simla-Garhwal, Jammu and Zaskar Range, Ladakh. Singh¹¹⁻¹³ also noted the absence of Palaeocene foraminiferal sequence in Kalkot-Beragua-Jangal-gali area of Jammu where Early Eocene foraminifera bearing rocks of Subathu Group conformably overly



FIGS. 1-10. Figs. 1, 2 and 10. *Nummulites discorbinus*, 1. axial section of No. IPE/B01/01/710, $\times 14.5$; Fig. 2. Axial section of No. IPE/B01/01/709, $\times 7.5$; 10. Equatorial section of No. IPE/B01/01/711, $\times 8.2$; Fig. 3. *Nummulites subataricus*, axial section of No. IPE/B01/01/712, $\times 12.1$; Fig. 4. *Rotalia trochidiformis*, axial section of No. IPE/B01/01/732, $\times 17.1$; Fig. 5. *Dictyoconoides flemingi*, axial section of No. IPE/B01/01/713, $\times 11.9$; Figs. 6, 7. *Lockhartia huntii* var. *pustulosa*, 6. Axial section of No. IPE/B01/01/714, $\times 16.3$; 7. Equatorial section of No. IPE/B01/01/715, $\times 14.8$; Figs. 8, 9. *Lockhartia huntii*, 8. Axial section of No. IPE/B01/01/716, $\times 15.6$; 9. Axial section of No. IPE/B01/01/717, $\times 12.0$.