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SPECTRAL STUDIES OF TRICHLOROACETATES OF LANTHANONS

THE halogen substituted acetates of *d*-transition elements have been extensively studied¹⁻². However, there has been only a very limited effort made in the study of halogen substituted acetates of lanthanons³⁻⁴. Trichloroacetates of lanthanons have been synthesized by Tilley *et al.*³ but no data have been reported on their spectral studies. The electronic and infrared spectra of these compounds are reported in this note.

Experimental

Trihydrated trichloroacetates were prepared by the method of Tilley *et al.*³. Electronic spectra were measured on Carl-Zeiss VSU-2 Spectrophotometer in water. IR spectra of the KBr pellets were run on Perkin-Elmer 621 Spectrophotometer. Magnetic properties of the compounds were measured by Gouy method at 295 K. The molar susceptibilities were corrected for the diamagnetism of the constituent atoms by means of Pascal's constant⁵.

Results and Discussion

COO⁻ stretching frequencies in acetates have been found to be sensitive to both coordination to a metal and substitution in the acetate group⁶⁻⁷. Comparing the values of ν_a COO⁻ in sodium trichloroacetate⁸, Cu(II) trichloroacetate² and lanthanon trichloroacetates we have observed that the value of ν_a COO⁻ changes considerably. Comparing the values of ν_a COO⁻ in sodium trichloroacetate and lanthanon analogue, there is sufficient change but its magnitude is less than that observed for copper analogue

indicating thereby that the lanthanon trichloroacetates form the bridge between highly ionic sodium trichloroacetate and covalent Cu(II) trichloroacetate. In lanthanon trichloroacetate themselves, the value of ν_a COO⁻ gradually increases which is in conformity of lanthanide contraction. In the lanthanon trichloroacetates the ν_a COO⁻ a strong band occurring at 1650–1655 cm⁻¹ shows a decrease while ν_s COO⁻ shows an increase as compared to sodium analogue, which can be interpreted in terms of bidentate structure for these trichloroacetates as suggested by Warriar *et al.*⁶⁻⁷ for Cu(II) trichloroacetates. Trichloroacetic acid and its anion show only high carbon halogen stretching frequencies⁸. Contrary to this the values for lanthanon trichloroacetates we find that the high carbon halogen frequencies are quite intense while lower are quite weak. This indicates that lanthanon trichloroacetates are most probably the mixtures of two conformations *trans* and *gauche* form on the same line suggested by Spinner⁸. Absorption between 500–400 cm⁻¹ in the spectra of lanthanon trichloroacetates probably arises from carbon halogen bending vibrations. Only two C–Cl₃ deformations are observed in Cu(II) trichloroacetate² while in lanthanon trichloroacetates four C–Cl₃ deformations are observed and the higher frequency bands are identified with asymmetric while those at lower frequencies are attributed to symmetric deformations.

TABLE I

Nephelauxetic ratio (β), covalency parameter (δ) and magnetic susceptibility data for trichloroacetates of lanthanons

Compound	β	δ (%)	Molar susceptibility $\chi_m^{\text{corr}} \times 10^6$ C.G.S. units	Magnetic moment μ_{eff} in B.M
Pr TCA	0.99447	+0.5560	5452	3.59
Nd TCA	1.00500	-0.4975	5288	3.54
Sm TCA	1.01165	-1.1516	1595	1.94

It has been shown by Karvaker⁹ that the band shape for hypersensitive transition can be correlated with the coordination number and ligand geometry on the lanthanide ion. The shape of the hypersensitive transition of Nd(III) trichloroacetate ($^4I_{9/2} \rightarrow ^4G_{5/2}, ^2G_{7/2}$) in water is quite identical with the bands of non-coordinated Nd (BrO₃)₃·9H₂O in water as well as in solid⁹ indicating thereby that these compounds are most likely non-coordinated.

It is, of course, risky to transfer conclusions from solution measurement to solid compounds. The values of nephelauxetic ratio (β) which is less than one and covalency parameter (δ) which is positive in Pr(III) trichloroacetate while in case of Nd and Sm(III) trichloroacetate β is more than one and δ is negative. The negative values of δ is quite surprising in view of highly coordinated nature of trichloroacetate grouping. Sinha¹⁰ also observed negative values for δ which he interpreted in terms of ionic character in the complexes as compared to aquo ion.

The magnetic susceptibilities of Pr, Nd and Sm(III) trichloroacetates have been measured and the values of magnetic moments of these derivatives have been found to be closer to the values reported by earlier workers¹¹⁻¹⁴.

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PILLOW BRECCIA FROM THE PRECAMBRIAN METABASALTS OF THE CHITRADURGA GREENSTONE BELT, KARNATAKA

PRECAMBRIAN greenstone belt of Chitradurga is dominantly composed of 2345 m.y. old metavolcanics associated with metasediments. The metavolcanic rocks are dominantly metabasalts, which exhibit a variety of volcanic structures like pillows, varioles, vesicles and amygdalites,² and volcanic bombs³. During a recent survey, the authors have come across pillow

breccias in the greenstone sequence of this belt. The authors are not aware of any reported occurrences of pillow breccias from here or other parts of India.

The pillow breccia reported here occurs close to the village of Kallehadlu, 14 kilometres south of Chitradurga town. The geological map (Fig. 1) shows the setting of the pillow breccia in the volcanic sequence. The pillow breccia is illustrated in Figs. 2a and 2b. The breccia, distributed in an area of 20 m × 30 m, is immediately associated with well jointed massive epidiorite. The pillow breccia and the associated epidiorites are underlain by pillowed metabasalts, which in turn are underlain by variolitic basalt. The volcanic rocks are associated with metagreywackes, quartz sericite schists and banded ferruginous chert, that are interbedded with lava flows.

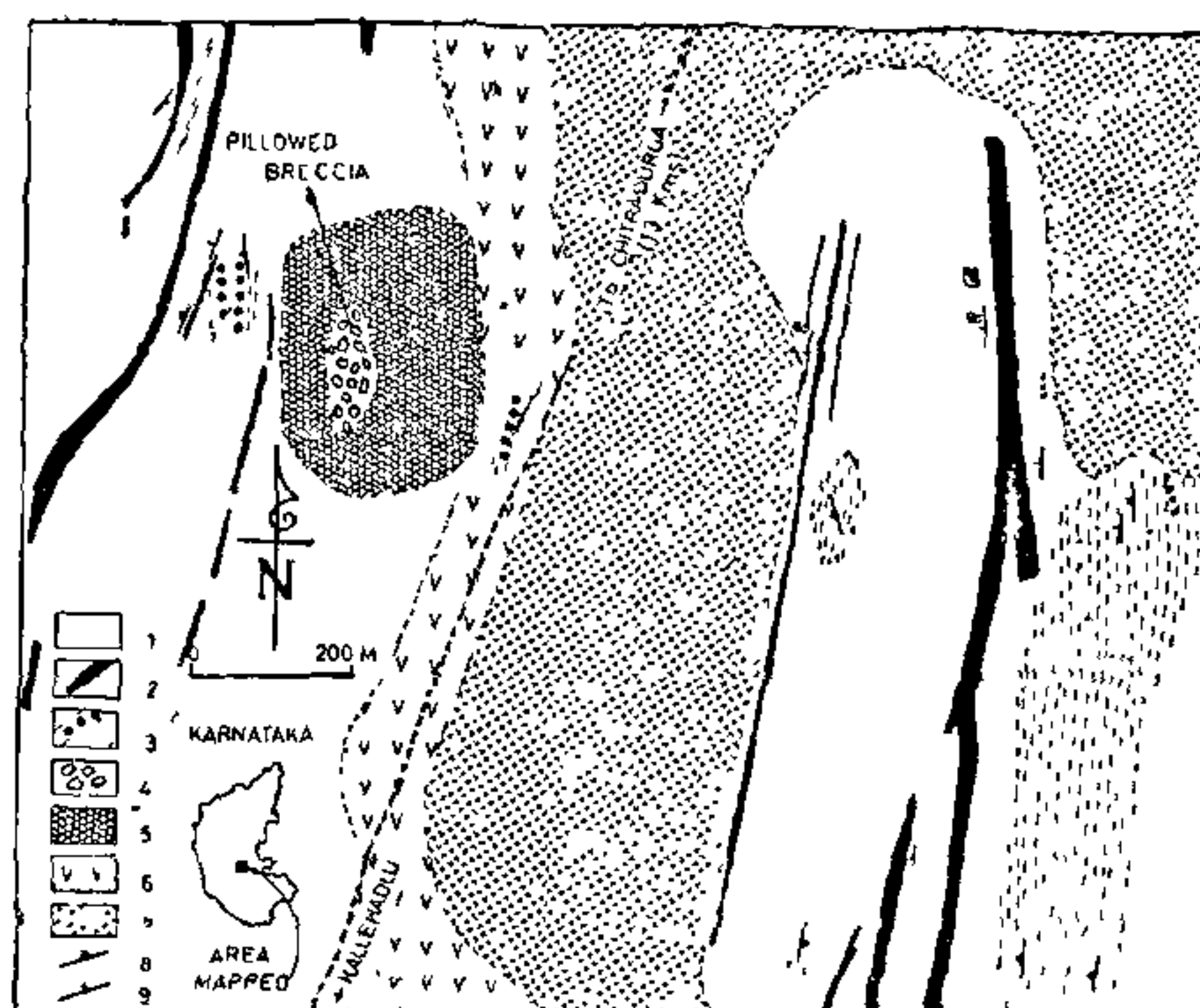


FIG. 1. Geological map of the pillow breccia locality near Kallehadlu village, Chitradurga greenstone belt, Karnataka.

Index: (1) Soil and rock debris. (2) Banded ferruginous chert. (3) Chlorite schist (Meta tuff) intercalated with chert bands. (4) Pillowed breccia. (5) Epidiorite intrusive. (6) Pillowed metabasalt. (7) Variolitic metabasalt. (8) Dip and strike of foliation. (9) Dip and strike of bedding.

Individual pillow breccia fragments have chilled margin all around, and possess radial cracks characteristic of pillow structures. Unlike in pillow lavas, there are not many vesicles immediately beneath the chilled margin, but, quite often a large cavity characterises the central portion of the breccia fragments (see top of Fig. 2a). As the name of structure implies, pillow-like fragments are angular or irregular. The size of the pillow breccia fragments varies from about 2.5 cm to 15 cm, although a few larger ones which are as much as 30 cm are noticed. Unlike in the pillow lavas, where the pillow structures predominate over the matrix, the matrix dominates over the pillow fragments in the pillow breccia.