Studies on Lanthanide(III) Hexamethylenedithiocarbamate Complexes

K K Dahiya & N K Kaushik*

Department of Chemistry, University of Delhi, Delhi 110 007

Received 10 June 1987; revised and accepted 9 September 1987

Hexamethylenedithiocarbamate complexes of the type \( \text{Ln} \left( \text{C}_6\text{H}_{12}\text{NCS}_2 \right) \) [where \( \text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Tb} \) and \( \text{Dy} \)] have been synthesized and characterized on the basis of elemental analysis, conductance measurements and magnetic, spectral (IR, UV, visible, \(^1\text{H} \) NMR) and fluorescence studies. IR and UV spectral studies show that the dithiocarbamate group behaves as a S-S bonding bidentate ligand.

The present note deals with the preparation and characterization of some lanthanide(III) hexamethylenedithiocarbamate complexes. Sodium hexamethylenedithiocarbamate was prepared by the modified method given by Gilman and Blatt. Anhydrous trichlorides \( (\text{MCl}_3) \) of the lanthanides \( (\text{M} = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Tb}, \text{Dy}) \) were prepared by the method reported by Taylor and Carter. All the complexes were prepared by a similar method. The complexes(I) were prepared, in anhydrous and inert atmosphere, by refluxing ethanolic solutions of the metal trichloride and the ligand in 1:3 stoichiometric ratio in nitrogen atmosphere with vigorous shaking. Solid crystals separated out, the solvent was removed under reduced pressure to about one third of its original volume. Anhydrous petroleum ether \((60-80^\circ \text{C})\) \((-30 \text{ ml})\) was added to it about one third of its original volume. These were recrystallized from acetonitrile.

Conductance measurements were carried out on an Elico conductivity bridge (model CM-82). IR of the compounds in nujol were recorded on a Shimadzu infrared spectrophotometer IR-435 in the range 4000-400 cm\(^{-1}\). The far IR spectra were recorded on a Perkin-Elmer 621 grating spectrophotometer. Perkin-Elmer UV-Vis spectrometer, model 554, was used for recording the UV and visible spectra of the compounds. The PMR spectra were recorded at room temperature on a Jeol FX-200 FT-NMR spectrometer at a spectral width of 1000 Hz. Fluorescence studies were carried out on a Jasco FP-500 spectrophotofluorometer. Gouy's method was chosen for the magnetic moment studies.

Molar conductance values of these complexes in \( 10^{-3} \text{M} \) nitrobenzene solution are of the order of 0.50 Ohm\(^{-1}\)cm\(^2\)mol\(^{-1}\), indicating that the complexes are non-electrolytes. The complexes are soluble in acetonitrile, methylene chloride and DMSO. The paramagnetic behaviour of the lanthanide(III) ions is consistent with the presence of unpaired \( 4f \) electrons. The magnetic moment, \( \mu_{\text{eff}} \) (B.M. at 300 K) values for the complexes are as follows: \( \text{La} \left( \text{dtc} \right)_3 \) diamag.; \( \text{Pr} \left( \text{dtc} \right)_3 \), 3.62; \( \text{Nd} \left( \text{dtc} \right)_3 \), 3.50; \( \text{Sm} \left( \text{dtc} \right)_3 \), 1.46; \( \text{Tb} \left( \text{dtc} \right)_3 \), 9.48; \( \text{Dy} \left( \text{dtc} \right)_3 \), 10.40.

All the complexes possess only one medium intensity band in their IR spectra at \( \sim 1000 \text{ cm}^{-1} \). This indicates the presence of a four-membered ring system and also supports the bidentate nature of dithiocarbamate ligand. The frequency of the thioureide band at \( \sim 1500 \text{ cm}^{-1} \) lies in between that of C-N \((1350-1250 \text{ cm}^{-1})\) and C=N \((1690-1640 \text{ cm}^{-1})\), which suggests that this band possesses double bond character. The non-ligand bands occurring at \( \sim 375 \text{ cm}^{-1} \) have been tentatively assigned to \( \nu(M-S) \) modes.

Since in lanthanide ions the \( 4f \) orbitals are effectively shielded by the \( 5s^25p^6 \) octet, the lines appearing in their absorption spectra arise from electronic transitions within the \( 4f \) levels, which are normally forbidden, but are allowed after the removal of degeneracy in the \( 4f \) orbitals by external crystal fields. The absorption bands in \( \text{Pr}(\text{III}), \text{Nd}(\text{III}), \text{Sm}(\text{III}), \text{Tb}(\text{III}) \) and \( \text{Dy}(\text{III}) \) appear due to the transitions from the ground levels \( ^2\text{H}_4, ^4\text{I}_{9/2}, ^6\text{H}_{5/2} \), \( ^7\text{F}_6 \) and \( ^6\text{H}_{15/2} \) respectively to the excited \( J \) levels of the \( 4f \) configuration. The states arising from various \( f \) configurations are only slightly affected by the surrounding ions and are practically invariant for a given ion in all of its compounds. Electronic spectral bands \( (\text{cm}^{-1}) \) with assignments for the complexes are presented in Table 1.

In the UV region an intense band appears at \( \sim 260 \text{ nm} \) (log \( e \) \( \sim 4.0 \)) due to the interligand \( \pi-\pi^* \) transition of the \( \text{N} \cdots \text{C} \cdots \text{S} \) group. The intraligand \( \pi-\pi^* \) transition of the \( \text{S} \cdots \text{C} \cdots \text{S} \) group generally appears as a shoulder and is associated with the inequivalence of the \( \text{C} \cdots \text{S} \) bonds of the ligand. Thus, in dithiocarbamate complexes this band is observed in cases where the dithiocarbamate moiety is bonded in equiv-
From the fluorescence spectra, quantum yield of fluorescence ($\phi_f$) has been calculated using a relative method and taking anthracene as the reference material. The areas under the emission curves for the standard and experimental samples were calculated by the planimetric integration method.

The quantum yields of fluorescence show deviation from unity. Thus, fluorescence remains the dominant but certainly not the exclusive mode of emission. The non-radiative processes like intersystem crossing and internal conversion are probably contributing to the emission process. The $\phi_f$ values are as follows: La(dtc)$_3$, 0.47; Pr(dtc)$_3$, 0.15; Nd(dtc)$_3$, 0.17; Sm(dtc)$_3$, 0.43; Tb(dtc)$_3$, 0.12; Dy(dtc)$_3$, 0.13; (dtc = C$_6$H$_{12}$NCS$_2$).

### References