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NOTE

Synthesis and Conductance Behaviour of Lanthanides(III) Complexes of 1,10-Phenanthroline and 2,2′-Bipyridyl

ALAKNANDA DODKEY-SUPEKAR* and G.S. NATARAJAN†
S.B. Education Society's Science College, Aurangabad-431 001, India

The synthesis and conductance behaviour of some lanthanide(III) complexes with nitrogen containing ligands such as 1,10-phenanthroline and 2,2′-bipyridyl have been carried out. These complexes showed the values of the equivalent conductances between 80-100 mhos cm^{-1} with suggested that the complex behaves as a 1:3 electrolyte.

Key Words: Conductance behaviour, Lanthanide(III) complexes, 1,10-Phenanthroline, 2,2′-Bipyridyl.

A few nitrogen donors complexes of lanthanides(III) to go into such relatively poorly explored areas as their conductance behaviour. The conductance behaviour of the pure lanthanides in the form of chlorides and sulphates are well investigated[1] and the results have been shown to adhere to expected theories in electrochemistry. However, no literature on the conductance behaviour of chelates of lanthanides with nitrogen donors have been reported.

The present work was carried out to prepare lanthanide(III) complexes with nitrogen containing ligands such as 1,10-phenanthroline and 2,2′-bipyridyl and characterize them using standard techniques before using them for study of their conductance behaviour in anhydrous methanol at room temperature.

All rare earth oxides used in this work were procured from M/s Indian Rare Earths Ltd., Kerala, India and were of 99.9 % purity. The corresponding chlorides of these rare earths were prepared using standard procedures[2]. The simple complexes of these rare earth chloride using 1,10-phenanthroline and 2,2′-bipyridyl were prepared by the method of Rao *et al.*[3]. All conductance measurements were carried out by dissolving the salt in absolute methanol and measuring its conductance using a Leeds and Northrup Students Potentiometer Catalog 7645 which has provisions to function as a Wheatston's Bridge coupled with an 1000 cycles/s oscillator and a dip type conductivity cell (M/s Toshniwal Brother, Mumbai, India).

†Priyadarshini Institute of Engineering and Technology, Nagpur-440 019, India.

The lanthanides complexes of 1,10-phenanthroline and 2,2′-bipyridyl were characterized and the results in given in Table-1. In all cases, it is found that this corresponded to a 1:1 complex of the metal to the ligand. The chloride is expected to be ionic in nature and was estimated directly by the adsorption indicator method using dichlorofluorescein indicator. That the chloride ions could be ionic chloride was confirmed by exchanging them through an anion exchanger when the $Ln(complex)^{3+}$ would exchange leaving the chloride in solution which could be easily estimated.

TABLE-1
CHARACTERIZATION OF LANTHANIDE(III) COMPLEXES OF 1,10-PHENANTHROLINE AND 2,2′-BIPYRIDYL

Complex	m.w.	Elemental analysis Calcd. (Found) %					WC
		C	H	N	M	Cl	(%)
$La(1,10\text{-phen})_2Cl_3\cdot 2H_2O$	677.86	42.48 (42.30)	2.95 (2.89)	8.26 (8.24)	24.03 (24.01)	15.71 (15.69)	5.31 (5.26)
$Pr(1,10\text{-phen})_2Cl_3\cdot 2H_2O$	679.86	42.36 (42.20)	2.94 (2.81)	8.23 (8.20)	24.25 (24.20)	15.66 (15.28)	5.29 (5.26)
$Nd(1,10\text{-phen})_2Cl_3\cdot 2H_2O$	682.70	42.18 (42.09)	2.92 (2.79)	8.20 (8.15)	24.42 (23.76)	15.59 (15.27)	5.27 (5.15)
$Sm(1,10\text{-phen})_2Cl_3\cdot 2H_2O$	688.86	41.80 (41.69)	2.90 (2.78)	8.12 (8.10)	25.31 (25.21)	15.46 (15.01)	5.22 (5.21)
$Gd(1,10\text{-phen})_2Cl_3\cdot 2H_2O$	695.71	41.39 (41.13)	2.87 (2.81)	8.04 (8.01)	26.05 (25.90)	15.30 (15.24)	5.17 (5.13)
$Dy(1,10\text{-phen})_2Cl_3\cdot 2H_2O$	700.96	41.08 (41.01)	2.85 (2.79)	7.98 (7.81)	26.60 (26.20)	15.19 (15.01)	5.13 (5.10)
$La(Bip)_2Cl_3\cdot 2H_2O$	593.78	40.41 (40.10)	3.36 (3.20)	9.43 (9.40)	27.43 (26.90)	17.93 (17.19)	6.06 (6.01)
$Pr(Bip)_2Cl_3\cdot 2H_2O$	595.78	40.28 (40.15)	3.35 (3.15)	9.39 (9.35)	27.67 (27.51)	17.87 (17.16)	6.04 (6.00)
$Nd(Bip)_2Cl_3\cdot 2H_2O$	599.12	40.05 (40.00)	3.33 (3.10)	9.34 (9.30)	27.83 (27.42)	17.77 (17.05)	6.00 (5.99)
$Sm(Bip)_2Cl_3\cdot 2H_2O$	605.28	39.65 (39.40)	3.30 (3.09)	9.25 (9.20)	28.79 (27.90)	17.59 (17.49)	5.94 (5.91)
$Gd(Bip)_2Cl_3\cdot 2H_2O$	611.63	39.23 (39.10)	3.26 (3.07)	9.15 (9.10)	29.63 (28.90)	17.42 (17.22)	5.88 (5.82)
$Dy(Bip)_2Cl_3\cdot 2H_2O$	617.38	38.87 (38.79)	3.23 (3.02)	9.07 (9.01)	30.20 (30.03)	17.25 (17.15)	5.83 (5.80)

WC = Water of crystallization

The presence of three Cl^- was detected in all cases studied. The water of crystallization, as lattice water, was confirmed by heating the samples uniformly to 170ºC and observing the loss in weight. It was confirmed that the complexes of the type $Ln(1,10\text{-phenanthroline})^{3+}$ and $Ln(2,2'\text{-bipyridyl})^{3+}$ are present as ionic species. The conductance studies in Table-2 reflect the results of such studies carried out on the pure lanthanide chlorides, the lanthanide-1,10-phenanthroline complex and the lanthanide-2,2′-bipyridyl complex in pure methanol. The trend of the conductance values with concentration followed the traditional Onsager equation namely

$$\Omega_c = \Omega_o + z_1 (C)^{0.5} + z_2 \cdot C$$

TABLE-2
CONDUCTANCE DATA FOR LANTHANIDE(III) COMPLEXES WITH 1,10-PHENANTHROLINE AND 2,2′-BIPYRIDYL IN METHANOL AT 25ºC

Complex	Ω_o (mhos cm^2)	Z_1	z_2	Regression coefficient (r^2)
$La(1,10\text{-phen})_2Cl_3 \cdot 2H_2O$	85.17	-1041.16	5072.62	0.9975
$Pr(1,10\text{-phen})_2Cl_3 \cdot 2H_2O$	74.80	-1025.80	6015.83	0.9845
$Nd(1,10\text{-phen})_2Cl_3 \cdot 2H_2O$	97.14	-1854.01	13737.85	0.9953
$Sm(1,10\text{-phen})_2Cl_3 \cdot 2H_2O$	89.41	-1306.51	7635.20	0.9986
$Gd(1,10\text{-phen})_2Cl_3 \cdot 2H_2O$	87.83	-1307.83	8633.31	0.9930
$Dy(1,10\text{-phen})_2Cl_3 \cdot 2H_2O$	69.09	-566.69	2157.30	0.9952
$La(Bip)_2Cl_3 \cdot 2H_2O$	98.12	-1446.49	7341.61	0.9854
$Pr(Bip)_2Cl_3 \cdot 2H_2O$	74.20	-748.41	3340.49	0.9861
$Nd(Bip)_2Cl_3 \cdot 2H_2O$	85.32	-1089.90	5829.95	0.9932
$Sm(Bip)_2Cl_3 \cdot 2H_2O$	75.72	-633.03	1445.24	0.9905
$Gd(Bip)_2Cl_3 \cdot 2H_2O$	125.52	-2122.80	12946.38	0.9822
$Dy(Bip)_2Cl_3 \cdot 2H_2O$	82.32	-708.29	1379.44	0.9560

The results were processed using standard computer programs available and values of z_1, z_2 and Ω_o tabluted. The regression coefficient was observed to be fairly good in all cases. When values of molar conductances calculated from estimated value of Ω_o for the hydrated chlorides were plotted against concentration, it is foud that it followed a trend similar trend as that reportd in literature except that values were marginally higher. For the complexes however as is to be expected from literature data the value of the equivalent conductances should lie between 80-100 mhos cm^{-1} provided the complex behaves as a 1:3 electrolyte.

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