

Inorganic Co-ordination Compounds of Tetravalent Cerium Complexes of Cerium (IV) Sulphate with Primary Aliphatic Amines

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Abstract

Some complexes of cerium (IV) sulphate with ammonia and primary aliphatic amines have been prepared. The molecular formulae on the basis of analysis turn out to be $Ce(SO_4)_2 \cdot 4$ amine. The complexes behave as electrolytes. The absorption spectra have been recorded and an interpretation is offered for possible transitions.

Lanthanides, and cerium in particular are receiving special attention these days. A number of complexes of latter with various ligands and anions have been reported¹⁻⁵). In the present paper some complexes of cerium (IV) sulphate with ammonia, methyl, ethyl, propyl and butylamine are being presented.

Experimental Section

I. Synthesis

a) Cerium (IV) sulphate — E. MERCK grade was directly used.

b) Complexes — All complexes were prepared by the following method.

One gm. of cerium (IV) sulphate was suspended in 30 cm³ of acetone and a little more than the calculated quantity of amine was added. The reaction mixture was shaken for six days. The resulting crystalline solid was filtered, washed repeatedly with acetone and dried over P_4O_{10} . The analytical results are given below.

1. Tetra (ammine) cerium (IV) sulphate — yellow in colour. Found Ce = 34.68%; H = 4.68%, N = 13.80%, $SO_4 = 48.00\%$; $H_{12}N_4S_2O_8Ce$ requires Ce = 34.98%, H = 2.94%, N = 13.99%, $SO_4 = 47.98\%$.

¹) F. A. HART and F. P. LAMING, *J. Inorg. Nucl. Chem.* **27**, 1825 (1965); *ibid.* **26**, 579 (1964).

²) S. P. SINHA, *J. Inorg. Nucl. Chem.* **27**, 115 (1965); *Spectrochim. Acta* **20**, 879 (1964).

³) S. P. SINHA, C. K. JORGENSEN and R. PAPPALARDO, *Z. Naturforsch.* **19a**, 434 (1964).

⁴) L. I. KONONEUKO and N. S. POLUEKTOV, *Russ. J. Inorg. Chem. (Engl. transl.)* **7**, 965 (1962).

⁵) R. A. CHUPAKHINA and V. V. SEREBRENNIKOV, *Russ. J. Inorg. Chem. (Engl. transl.)* **7**, 1406 (1962).

2. Tetra (methylamino) cerium (IV) sulphate — light yellow in colour. Found Ce = 30.46%, C = 10.20%, H = 4.10%, N = 12.30%, SO₄ = 42.12%; C₄H₂₀N₄S₂O₈Ce requires Ce = 30.68%, C = 10.52%, H = 4.38%, N = 12.29%, SO₄ = 42.09%.

3. Tetra (ethylamino) cerium (IV) sulphate — yellow in colour. Found Ce = 27.12%, C = 18.44%, H = 5.26%, N = 10.70%, SO₄ = 37.30%; C₈H₂₈N₄S₂O₈Ce requires Ce = 27.32%, C = 18.74%, H = 5.46%, N = 10.93%, SO₄ = 37.44%.

4. Tetra (n-propylamino) cerium (IV) sulphate — yellow in colour. Found Ce = 24.43%, C = 25.80%, H = 6.01%, N = 9.66%, SO₄ = 34.70%; C₁₂H₃₆N₄S₂O₈Ce requires Ce = 24.64%, C = 25.34%, H = 6.33%, N = 9.85%, SO₄ = 34.58%.

5. Tetra (n-butylamino) cerium (IV) sulphate — mustered in colour. Found Ce = 22.30%, C = 30.20%, H = 7.15%, N = 8.58%, SO₄ = 30.43%; C₁₆H₄₄N₄S₂O₈Ce requires Ce = 22.43%, C = 30.76%, H = 7.05%, N = 8.97%, SO₄ = 30.76%.

II. Analysis

Metallic content was estimated by dissolving complex in nitric acid and precipitating cerium as Ce(IO₃)₄. Carbon, hydrogen and nitrogen were estimated microanalytically and sulphate as BaSO₄.

III. Conductivity

Measurements were done in formamide at a conc. of 10⁻⁴ M. The cell used had a cell constant of 0.0232.

IV. Spectra measurements-Spectra

Spectra were recorded on a Unicam S.P. 500 spectrophotometer using formamide as the solvent.

Discussion

Results of analysis indicate molecular formula to be Ce(SO₄)₂ · 4 amine. The values of molar conductance in formamide ranges from 40 to 50 mhos, which is same as that for a complex dissociating in three ions⁶). The general formula is thus to be written as [Ce(amine)₄](SO₄)₂.

The absorption spectrum shows a single band in the near visible region in the vicinity of 350 mμ. The absorption bands of different complexes of a given lanthanide element with a given oxidation number, have nearly the same position, only dependent on central atom. The bands are very much less influenced by the ligand fields than are the spectral bands of "d" transition metal ions. It is thus observed from table 1 that irrespective of the amine ligand field around the metal, the bands are usually at the same position. These narrow bands can be identified as internal transitions in the partly filled 4f shell.

⁶) R. S. NYHOLM, J. chem. Soc. London 1714 (1957).

Table 1
Absorption spectral results

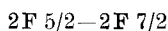
Compound	δ	Intensity ϵ_0	λ max in $m\mu$	Frequency in cm^{-1}
1. Cerium (IV) sulphate	0.016KK	0.02	355	28.600
2. Tetrammine cerium (IV) sulphate	0.105KK	2.42	350	28.620
3. Tetra (methylamino) cerium (IV) sulphate	0.110KK	10.00	345	29.000
4. Tetra (ethylamino) cerium (IV) sulphate	0.105KK	12.50	355	28.600
5. Tetra (n-propylamino) cerium (IV) sulphate	0.015KK	0.05	355	28.600
6. Tetra (n-butylamino) cerium (IV) sulphate	0.200KK	0.08	352	28.608

The $4f^n$ transitions of lanthanides are all typical and conspicuous case of the approximate spherical symmetry in chemistry. The absorption bands of the above complexes are characterised by their narrowness δ between 0.016 and 0.3 KK, as the FRANK-CONDON principle enforces the vibrational excitation of the nearly parallel potential curves. Their low intensity ϵ_0 between 0.01–15, all of which are LAPORTE-forbidden and their relative small shift due to nephelantetic effect and bands splitting due to ligand field effects.

LAPORTE-allowed $f^n \rightarrow f^{n-1}d$ transitions can be observed in cerium. Energy levels are

2F 5/2	0	2D 3/2	49.74KK
2F 7/2	2.25	2D 5/2	52.23KK

The bands which can thus be theoretically said to be arising due to following transition



can be more correctly interpreted by saying that they are actually electron transfer bands and not shifted internal transitions of ligands.

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