

temperature. The positive temperature coefficient for both the acids can be explained¹⁰ on the basis that increase of temperature (a) causes the rupture of hydrogen bonds in the diethylene glycol molecules and (b) will facilitate the rotation of solvent molecules by increasing the force causing the rotation. Thus both the effects increase the mobility of the protons. The ion size parameter obtained for hydrogen chloride is of the same order as in the case of DMSO-water mixtures¹¹ and is unaffected by temperature changes. The near constancy of the Walden product (Table 2) is most presumably due to the compensating contribution of the positive temperature coefficient of conductance of the acids by the negative temperature coefficient of the viscosity of the solvent. The slight decrease of this quantity with increase in temperature is in agreement³ with the observations on hydrogen chloride in propanol-water mixtures.

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References

1. JANZ, G. J. & DANYLUK, S. S., *Chem. Rev.*, **60** (1960), 209.
2. GOFFREDI, M. & SHEDLOVSKY, T., *J. phys. Chem.*, **71** (1967), 2182.
3. SPIVEY, H. O. & SHEDLOVSKY, T., *J. phys. Chem.*, **71** (1967), 2165.
4. SELVARAJAN, V. M. & KALIDAS, C., *Trans. SAEST*, **9** (1974), 111.
5. KALIDAS, C. & SRINIVAS RAO, V., *J. chem. Engng Data*, **19** (1974), 201.
6. CHRIST, O. & ELIAS, H., *Chem. Ber.*, **99** (1966), 1.
7. GALLANT, R. W., *Hydrocarbon process.*, **46** (1964), 183.
8. FUOSS, R. M., ONSAGER, L. & SKINNER, J. F., *J. phys. Chem.*, **69** (1965), 2581.
9. EVANS, D. F. & KAY, R. L., *J. phys. Chem.*, **70** (1966), 366.
10. EWELL, R. H. & EYRING, H., *J. chem. Phys.*, **5** (1937), 726.
11. BOLZAN, J. A. & ARVIA, A. J., *Electrochim. Acta*, **15** (1970), 39.

Stability Constants of Chelates of Solochrome Dark Blue (Calcon) with La(III), Pr(III), Nd(III), Gd(III), Tb(III), Dy(III) & Ho(III)

J. R. NARKHEDE & G. S. NATARAJAN*

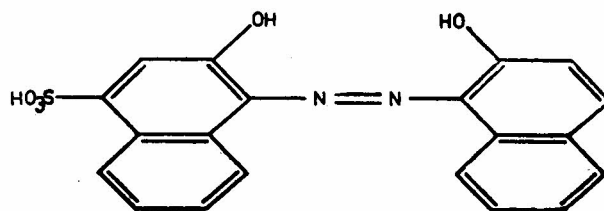
Inorganic Chemistry Laboratory, Laxminarayan Institute of Technology, Nagpur University, Nagpur

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The stability constants of 1:1 complexes of solochrome dark blue (calcon) with a few lanthanides have been determined potentiometrically in aq. dioxane (50%, v/v) using the Irving Rossotti titration technique.

SOLOCHROME Dark Blue (Calcon) has been widely employed as a complexometric reagent¹. The compound in view of the hydroxy groups ortho to the azo group form well defined complexes with several metal ions²⁻⁴. Complexes of calcon (I) with La(III) were first reported by Rehman *et al.*⁵. In

*Present address: Max Plank Institute Für Kohlenfurschung, 433, Mulheim, Ruhr, West Germany.



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the present note, we have determined the stability constants of the chelates of calcon with other lanthanides in aq. dioxane employing Irving and Rossotti⁶ titration technique.

Dioxane was purified by recommended procedure⁷. Carbonate-free sodium hydroxide⁸ (E. Merck, 0.4M) was standardized against solid potassium hydrogen phthalate (BDH AnalaR). Sodium salt of calcon (BDH) was purified as the corresponding acid by the method of Langmyhr⁹. The purified sample was stored in an anhydrous calcium chloride desiccator.

Solutions of the ligand (0.005M) were obtained by dissolving it in aq. dioxane (50%, v/v) and standardized potentiometrically. Rare earth metal oxides (Indian Rare Earths, Kerala, purity > 99.9%) were used in the form of their nitrates for the preparation of stock metal ion solutions in doubly distilled water. All metal ion stock solutions were 0.00165M in 0.05M perchloric acid (Riedel, Germany) and their metal ion contents were estimated by the gravimetric method¹⁰.

Systronics pH-meter (type 322-1, accuracy ± 0.05 pH units) using a glass calomel assembly calibrated at the working temperatures¹¹ was used to measure the apparent pH.

The ligand to metal ratio was kept around 3:1 in all titrations. All experiments were performed at 30°, 40° and 50° and at $\mu = 0.1$ (NaClO₄) under oxygen-free nitrogen presaturated with 50% (v/v) aq. dioxane.

As one of the -OH groups of the reagent dissociates at higher pH, the value obtained using the potentiometric method was checked spectrophotometrically¹². Values of the formation functions \bar{n}_A , \bar{n} and $\bar{p}L$ were calculated using the standard expressions⁶.

The values of $\log \bar{p}K_1^H$ and $\log \bar{p}K_2^H$ obtained from the \bar{n}_A versus pH (meter reading) curves were refined by (i) interpolation at half \bar{n}_A values and (ii) interpolation at various \bar{n}_A values. Stability constants

TABLE 1 — STABILITY CONSTANTS AND ΔF OF CHELATE FORMATION

(Temp. 30°; $\mu = 0.1$)

M ³⁺	log K_1	$-\Delta F$ kcal/mole
La	9.86	13.67
Pr	10.47	—
Nd	10.49	14.54
Gd	11.52	15.97
Tb	12.05	16.71
Dy	11.94	16.55
Ho	12.13	16.82

of metal complexes ($\log K_1$) were obtained from the \bar{n} versus pL curves and treated by the same methods. The values ΔF° of chelation were obtained by the temperature variation of stability constants (Table 1).

The ligand calcon (I) has three dissociable protons. The proton of the $-\text{SO}_3\text{H}$ group was assumed to be completely dissociated under the experimental conditions as no detectable lowering of the meter reading was observed when the ligand was added to the perchloric acid solution. The values of $\log pK_1^H$ and $\log pK_2^H$ at 30° are 11.28 and 8.23 respectively. The latter value is due to the dissociation of $-\text{OH}$ group meta to the sulphonic acid group¹³.

The maximum value of \bar{n} was 0.95 at an apparent pH 6.5 which approximately is the hydrolysis region of the rare-earth metal ion. Regions above this value were not employed for calculations. Below this value it may hence be inferred that a 1:1 metal chelate of calcon with rare-earth metal ion is formed by bonds between metal ion and the oxygen of the *o*-hydroxy group as well as the azo group; which is evident from the analogous chelates^{14,15}. The values of $\log K_1$, the stability constant for formation of a 1:1 chelate, refined by the methods outlined above, show trend similar to that observed earlier.

A linear graph between $\log K_1$ and Z^2/r^{3+} (r is the radius of the metal ion) for various rare earth metals shows that the metal-calcon bond is essentially ionic in character¹⁶.

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References

1. VOGEL, A. I., *A text book of quantitative inorganic analysis* (Longmans, Green, London), 1964, 427.
2. PETERS, L., ABELL, P. M. & WATSON, R. W., *Kolorisat Artesito*, **6** (1964), 394.
3. DEAN, J. A. & BRYAN, H. A., *Analytica Chim. Acta*, **16** (1957), 94.
4. KORKISH, J., *Z. analyt. Chem.*, (1960), 176.
5. REHAMAN, S. M. F., AHMED NASEER & AHMED JAMIL, *J. Indian chem. Soc.*, **45** (1968), 531.
6. IRVING H. M. & ROSSOTTI, H. S., *J. chem. Soc.*, (1954), 2904.
7. VOGEL, A. I., *A text book of practical organic chemistry* (Longmans, Green, London), 1961, 177.
8. VOGEL, A. I., *A text book of quantitative inorganic analysis* (Longmans, Green, London), 1964, 239.
9. LANGMYHR, F. J., KLAUSEN, K. S. & NAURI, M. H., *Analytica Chim. Acta*, **57** (1971), 342.
10. TOPP, N. E., *The chemistry of the rare earth elements* (Elsevier, London), 1965, 115.
11. ALBERT, A. & SERJEANT, E. P., *The determination of ionization constants* (Chapman & Hall, London), 1971, 104.
12. ALBERT, A. & SERJEANT, E. P., *The determination of ionization constants* (Chapman & Hall, London), 1971, 44.
13. LINDSTORM, F. & EDWARDS, A., *Talanta*, **20** (1973), 589.
14. PICKERING, W. F., *Modern analytical chemistry* (Marcel Dekker, New York), 1971, 366.
15. *Recent progress in the chemistry of natural and synthetic colouring matters and related fields*, edited by T. S. Gore, B. S. Joshi, S. V. Sunthakar & B. D. Tilak (Academic Press, New York and London), 1962, 459.
16. INGLE, D. B. & KHANOLKAR, D. D. *J. Indian chem. Soc.*, **50** (1973), 190.

N-Benzoyl-N-phenylhydroxylamine & Cyclohexanol Derivatives of Ti(IV)*

S. K. PANDIT & C. GOPINATHAN

National Chemical Laboratory, Poona 8

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N-Benzoyl-N-phenylhydroxylamine forms chelates with titanium tetrachloride and isopropyl titanate with the elimination of hydrogen chloride and isopropanol respectively. The isopropoxy derivative reacts further with bidentate ligands like salicylaldehyde, acetylacetone, benzoylacetone, dibenzoylmethane and 8-hydroxyquinoline. Similarly cyclohexanol derivatives of titanium chelates are obtained from cyclohexyl titanate or dichlorodicyclohexanoxytitanium and chelating ligands. Infrared spectra of these compounds have been studied and their molecular weights determined.

N-BENZOYL N-phenylhydroxylamine (LH) and its analogues are widely used as analytical reagents¹⁻⁵ in spectrophotometric and gravimetric estimation of metals. Its use in the extraction of metals⁵ is attributed to the formation of stable chelates, and to its selective complexing properties. Nesmeyanov⁶ was the first to report the preparation of cyclohexyl titanate; some more cyclohexyl derivatives are briefly described in literature^{7,8}. Our interest in the study of titanium chelates led us to prepare Ti(IV) complexes of LH and cyclohexanol.

Two chloro-derivatives, $\text{TiCl}_3(\text{L})$ and $\text{TiCl}_2(\text{L})_2$ were prepared from the reaction of the ligand with titanium tetrachloride. As expected, the ligand replaced both the alkoxy groups of *bis*-(salicylaldehyde)diisopropoxytitanium giving *bis*-(L)*bis*-(salicylaldehyde)titanium. When reacted with isopropyl titanate, the ligand (LH), gave *bis*-(L)diisopropoxytitanium. Chelating ligands like salicylaldehyde, acetylacetone, benzoylacetone, dibenzoylmethane and 8-hydroxyquinoline replaced both the alkoxy groups of *bis*-(L)diisopropoxytitanium. (L)Trichlorotitanium also reacted with salicylaldehyde giving a mixed dichloro derivative. Ammonia was absorbed and tenaciously retained by *bis*-(L)dichlorotitanium in ether forming *bis*-(L) $\text{TiCl}_2 \cdot 4\text{NH}_3$. The compounds prepared are listed in Table 1.

Cyclohexanoxy groups of cyclohexyl titanate were replaced by chelating ligands giving condensed complexes containing Ti-O-Ti bonds. Identical compounds were obtained when dichlorodicyclohexanoxytitanium was reacted with chelating ligands in presence of ammonia e.g., salicylaldehyde gave a product with the formula $[(\text{C}_6\text{H}_{11}\text{O})(\text{C}_7\text{H}_5\text{O}_2)_2\text{Ti}]_2\text{O}$. The new compounds obtained are listed in Table 2. The composition of these products was determined by elemental analysis and molecular weight determinations. The cyclohexanoxy derivatives and the ligand substituted alkoxytitanium compounds had good solubilities in boiling benzene and were found to be monomeric in the boiling solvent.

The νOH bands found in the free ligand at 3105 cm^{-1} are completely absent in the complexes.

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