

characteristic absorption bands at 3170 cm^{-1} , 1720 cm^{-1} and 1700 cm^{-1} for $>\text{NH}$, $>\text{C}=\text{O}$ and $>\text{C}=\text{O}$ groups respectively. The presence of additional bands, one at 3170 cm^{-1} in $>\text{NH}$ region and another at 1700 cm^{-1} in carbonyl region clearly indicate the attachment of the isatino carbonyl group with 5-position of the thiazolidonyl nucleus.

EXPERIMENTAL

All melting points were taken by capillary method and are uncorrected. The purity of the products was tested by thin layer chromatography (TLC). *Varian A60 D* model was used for recording of NMR spectra, *Perkin-Elmer 257* for IR and a *Coleman Analyzer* for analyses.

3-Benzyl-2-*p*-bromophenylimino-4-thiazolidone—A mixture of *N*-benzyl-*N'*-*p*-bromophenyl thiocarbamide (16.05 g), monochloroacetic acid (5 g), fused sodium acetate (8 g) and absolute alcohol (50 ml) was refluxed on a water-bath for 14–16 hours. After distilling off ethanol, the substance was washed with hot water when a gummy product was obtained. It was solidified on keeping overnight in contact with cold water and recrystallised from ethanol, yield 89%, mp 103° . TLC: $R_f = 0.27$ (Benzene-Ether, 3:1). *Anal.* Calcd. for $\text{C}_{16}\text{H}_{13}\text{N}_2\text{OSBr}$: N, 7.75; S, 8.86. Found: N, 7.61; S, 8.78%. IR $\nu_{\text{max}}^{\text{nujol}}$ cm^{-1} : 1730s, 1635s, 1590s, 1495s. NMR (CDCl_3): 3.80 (2H, s) for methylene protons of the thiazolidonyl nucleus, 5.10 (2H, s) for benzyl methylene protons and 7.35 for aromatic protons (9H, m).

Similarly, other required 3-benzyl-2-arylimino-4-thiazolidones were prepared by using their respective thiocarbamides.

Indole-(3)-[2-*p*-bromophenylimino-4-benzyl-4-thiazolidone-(5)] indigo—A mixture of 3-benzyl-2-*p*-bromophenylimino-4-thiazolidone (3.6 g), isatin (3 g), anhydrous sodium acetate (5 g), acetic acid (35 ml), and acetic anhydride (2 ml) was refluxed on an oil-bath for 3–4 hrs at $150\text{--}160^\circ\text{C}$. The reaction mixture was poured into excess of water. It was filtered, washed with water, dilute acetic acid and finally with ethanol. It was recrystallised from acetic acid, yield 87%, mp 279° . TLC: $R_f = 0.68$ (Benzene-Ether 3:1). *Anal.* Calcd. for $\text{C}_{24}\text{H}_{16}\text{N}_3\text{O}_2\text{SBr}$: N, 8.57; S, 6.53. Found: N, 8.37; S, 6.29%. IR $\nu_{\text{max}}^{\text{nujol}}$ cm^{-1} : 3170 w, 1720 m, 1700 s, 1640 s and 1585 s.

Likewise, other indole-(3)-[2-arylimino-3-benzyl-4-thiazolidone-(5)] indigos were prepared. Their yields, melting points, R_f values, analytical and spectral data are recorded in Table I.

The screening programme of these compounds are in progress.

ACKNOWLEDGEMENT

The authors are grateful to Prof. P. N. Bhargava for his keen interest and Prof. G. B. Singh for providing necessary facilities. Financial assistance by PGIIM, B.H.U., India to I.C.T. and by CSIR, New Delhi, to R.S. is also gratefully acknowledged.

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A NON-DESTRUCTIVE METHOD FOR THE DETERMINATION OF LANTHANUM AND COPPER USING A LOW-FLUX NEUTRON SOURCE

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ABSTRACT

The possibility of using a low-flux $\text{Am}^{241}\text{-Be}$ neutron source for the determination of lanthanum and copper by non-destructive neutron activities analysis when present together has been investigated.

LOW flux neutron sources are being used for the Neutron Activation Analysis^{1–11}. A 5-Ci $\text{Am}^{241}\text{-Be}$ neutron source employed for the analysis of important elements in various substances was employed in this work.

Since the flux of this neutron source is small (10^4 neutrons $\text{cm}^{-2}\text{ sec}^{-1}$), one needs large quantity of sample for irradiation in order to obtain reasonable

amount of radioactivity for accurate measurement. Large quantity of sample causes self-shielding of neutrons during irradiation and self-scattering and self-absorption of radiation during counting. In view of this difficulty, known amounts of the element to be determined are added to the sample and then irradiated. This procedure limits the volume of the sample and yet produces considerable amount of radioactivity

in the sample. In this method, the samples are irradiated for a long time (6 times the half life of the isotope formed) in order to get saturation activity which is the highest activity one can get with a given neutron source. Any further delay in the measurement is of no advantage. Hence we have employed graphical method which finds application when the gamma ray peaks corresponding to isotopes of two different elements overlap in the gamma ray spectrum. We have found that the graphical method gives better results than the ordinary comparator method^{11,10}.

When a sample containing both lanthanum and copper is irradiated using thermal neutrons, both lanthanum and copper get activated. The nuclear data for lanthanum and copper are given in Table I.

TABLE I
 Nuclear data for lanthanum and copper

Element	Isotope	% abundance	Thermal neutron cross-section (barns)	Half life of isotope formed
Cu	Cu ⁶³	69.1	4.7	12.74 h (Cu ⁶⁴)
	Cu ⁶⁵	30.9	1.9	5.1 min (Cu ⁶⁶)
La	La ¹³⁹	99.91	9.1	40.2 h (La ¹⁴⁰)

La¹⁴⁰ gives four peaks of energies 0.328, 0.487, 0.815 and 1.596 MeV and Cu⁶⁴ gives two peaks of energies 0.511 MeV and 1.34 MeV. But the 1.34 MeV peak of Cu⁶⁴ is not clearly seen in the spectrum. If NaI (TI) crystal is used as detector the 0.487 and 0.511 MeV peaks which are due to La¹⁴⁰ and Cu⁶⁴ respectively merge together and appear as a single peak. So determination of either lanthanum or copper in substances where they are present together becomes difficult. For such cases, we have devised a method to determine both these elements simultaneously. We have used lanthanum cuprate (La₂CuO₄) as a representative example to demonstrate the applicability of our method.

EXPERIMENTAL AND RESULTS

Two sets of standard samples are prepared in such a way that the amount of La₂CuO₄ presents in each sample is the same (0.4 gm) but vary in the amounts of Cu O (0.05-0.35 gm) in one case and La₂O₃ (0.05-0.35 gm) in the other. These two sets of samples are irradiated in the thermal neutron source in the region of constant neutron flux (≈ 10⁴ n/cm² - sec.) for 10 days in order that La¹⁴⁰ also attains the saturation activity. However irradiation for a period of 5 days (3 half lives) can also be employed.

After irradiation, the activities of the samples are measured by means of a 400 channel gamma-ray pulse height analyser (Frieske and Hoepfner) using a

2" x 2" NaI (TI) crystal as detector. The counting time is kept at 30 min in every case.

In the case of CuO addition samples, the peak fractions of the merged peak are calculated by means of Covell's method^{12,8} whereas in the case of La₂O₃ addition samples, the peak fractions of both the merged peak as well as the 1.596 MeV peak of La¹⁴⁰ are calculated. The peak fraction of the 1.596 MeV peak in the case of La₂O₃ addition samples is plotted against the amount of lanthanum added to the same amount of La₂CuO₄. A straight line plot (A) is obtained. The intercept of the plot "A" corresponds to the counts due to La present in La₂CuO₄. Using this intercept value, the amount of lanthanum (y) present in the La₂CuO₄ is read from plot A.

The peak fraction of the merged peak in the case of La₂O₃ addition samples, is plotted against the amount of lanthanum added. A straight line plot (B) is obtained. The intercept corresponds to the combined activity due to the lanthanum and copper present in La₂CuO₄. From this plot B, the change in peak fraction for 1 gm. of lanthanum is calculated. Similarly, the change in peak fraction per 1 gm copper is calculated from plot C which is obtained by plotting the peak fraction of the merged peak against the amount of copper added in the case of CuO addition samples. The intercept values of plots B and C should be equal.

Now, if "a" is the change in peak fraction per 1 gm of copper and "b" is that per 1 gm of lanthanum and if "x" and "y" are the amounts of copper and lanthanum respectively present in the La₂CuO₄,

$$N = a x + b y \tag{1}$$

where "N" is the intercept value obtained either from plot B or C. "a" and "b" are calculated from plots B and C respectively and "y" has been calculated from plot A. By using equation (1), the amount of copper present in La₂CuO₄ is calculated. A representative set of results obtained is given in Table II.

TABLE II

Results obtained for the determination of lanthanum and copper in La₂CuO₄

Sl. No.	% Copper		% Lanthanum	
	Theoretical	Found	Theoretical	Found
1.	15.68	15.24	68.53	69.12
2.	"	15.63	"	68.13
3.	"	16.02	"	68.9
4.	"	15.94	"	69.0

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ZINC(II) COMPLEXES WITH NITROGEN DONOR CHELATING LIGANDS

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ABSTRACT

Complexes of zinc (II) thiocyanate with nitrogen donor chelating ligands like orthophenanthroline, 5-nitroorthophenanthroline, 2, 9-dimethylorthophenanthroline, 2, 2'-dipyridyl, and 8-aminoquinoline have been synthesized and characterized by elemental analysis, infrared spectra and conductance measurements. Although in the synthesis of the complexes 1:1 metal:ligand ratio was maintained all the ligands form 1:2 metal complexes of the type $Zn(NCS)_2(AA)_2$ except 2, 9-dimethylorthophenanthroline which forms 1:1 complex, $Zn(NCS)_2(2,9\text{-dimethylorthophenanthroline})$. The complexes are insoluble in common non-coordinating solvents and do not melt sharply. The infrared spectral data indicate the presence of bridging thiocyanate bonding. The complexes are soluble in coordinating solvent, dimethylsulfoxide and exhibit molar conductance values attributable to 1:1 electrolyte. The breaking of the polymeric structure occurs in dimethylsulfoxide and formation of complexes of the type $[Zn(NCS)(DMSO)(2,9\text{-dimethylorthophenanthroline})]NCS$ and $[Zn(NCS)(DMSO)(AA)_2]NCS$ is suggested. The reaction of zinc (II) thiocyanate with ethanolic solution of biguanide leads to the isolation of bis (biguanide) zinc(II).

INTRODUCTION

THE ligands orthophenanthroline, 5-nitroorthophenanthroline, 2,9-dimethylorthophenanthroline, 2,2'-dipyridyl and 8-aminoquinoline contain N-C-N chelating group in common and are known to form mono, bis and tris complexes with metal ions^{1,2}. In the literature there is no record of mono complexes of these ligands with zinc(II) thiocyanate and the work described here deals with such complexes. The presence of thiocyanate groups in the complexes gives an added opportunity to find out the nature of bonding of the thiocyanate groups in the complexes. We reacted zinc(II) thiocyanate and the above heterocyclic amine ligands in 1:1 ratio in ethanolic medium, and, only in the case of 2,9-dimethylorthophenanthroline, we were able to prepare the desired mono complex. In all other cases (orthophenanthroline, 5-nitroorthophenanthroline, 2, 2'-dipyridyl and 8-aminoquinoline) we obtained bis complexes. A similar reaction with biguanide $[H_2N-C(=NH)-NH-C(=NH)-NH_2]$ led to the isolation of bis (biguanide)

zinc(II). The complexes have been characterized by elemental analysis, conductance and infrared spectral measurements.

EXPERIMENTAL

Materials and Methods

Zinc(II) thiocyanate and 8-aminoquinoline were obtained from Pfaltz and Bauer Inc. (U.S.A.). Orthophenanthroline, 5-nitroorthophenanthroline, 2,9-dimethylorthophenanthroline and 2, 2'-dipyridyl were supplied by G. Frederick and Smith Chemical Co. (U.S.A.). Biguanide was purchased from Aldrich Chemical Co. (U.S.A.). Zinc was estimated complexometrically with EDTA after igniting the complexes to ZnO and dissolving ZnO in dilute HCl. Carbon, hydrogen and nitrogen were determined microanalytically. Conductance measurements (25° C) were done in DMSO with Radcliff type OK 102/1 conductivity bridge and a dip type cell which was calibrated with KCl solutions. Infrared spectra were recorded in KBr pellets on Perkin Elmer Model 21 and 237 infrared spectrophotometers and