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# Some Thermogravimetric and Gas Chromatographic Studies of Copper (II) and Nickel (II) Complexes of *meso* and DL-*Bis*(Acetylacetone) Stilbenediimine

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ABSTRACT. *Bis* (acetylacetone) *meso*-stilbenediimine and *bis* (acetylacetone) DL-stilbenediimine form coloured copper (II) and nickel (II) chelates. Copper (II) complexes are not sensitive spectrophotometrically, but the nickel complexes show reasonable sensitivity. Similarly TG and DTG studies indicate that nickel complexes are relatively more volatile and thermally stable than corresponding copper chelates. The metal complexes can easily be gas chromatographed from OV101, 3% on chromosorb (80-100mesh size) column. Calibration range, detection limits and resolution of copper and nickel complexes are reported. The nickel complexes also show higher sensitivity with lower detection limit at ng levels than corresponding copper complexes.

The Schiff bases *bis*(acetylacetone) ethylenediimine and *bis*(acetylacetone) propylenediimine have been extensively studied as complexing (Ueno and Martell 1957; McCarthy and Martell 1955, Calligaris *et al.* 1972, Singh and Tandon 1978) and gas chromatographic reagents for the determination of copper, nickel, vanadium, palladium and platinum metal ions. The complexes can be selectively extracted into water immiscible organic solvents and gas chromatographic procedures have been developed, which enable the detection and determination of these metal ions at ng levels (Belcher *et al.* 1971, 1973a, 1973b, Uden and Henderson 1974, 1977).

The *bis*(acetylacetone) *meso*-stilbenediimine (*meso*-$SDA_2$) and *bis*(acetylacetone) DL-stilbenediimine (DL-$SDA_2$) and their copper (II), nickel (II) and cobalt (II) and oxovanadium complexes have been reported (McCarthy and Martell 1967, Pasini and Gullotti 1974, Kanatomi *et al.* 1976), but their potentials as gas chromatographic reagents have not been evaluated. This paper reports the thermogravimetric and gas chromatographic behaviour of copper and nickel complexes and compares their GLC reponses with that of *bis*(acetylacetone) ethylenediimine (en$A_2$).

## Experimental

The reagents *meso*-SD$A_2$, DL-SD$A_2$ and en$A_2$ and their copper and nickel complexes were prepared by reported methods (Belcher *et al.* 1973a&b). Spectrophotometric studies were carried out with a Hitachi 220 spectrophotometer. TG and DTG were recorded on a Stanton TG77 Thermal Analyser using 10mg sample with a heating rate of 20°C/min in a flowing nitrogen atmosphere 6-10cm$^3$/min by Elemental Micro-Analysis Ltd, U.K.

A Hitachi 163 Gas Chromatograph equipped with a flame ionization detector was used throughout the investigation. Stainless steel column 2mx3mm and 3mx3mm filled with OV101, 3% on chromosorb (80-100mesh size) and OV1, 3% on Uniport (80-100mesh size) were used.

Sublimation studies were carried out in sublimation apparatus immersed in oil bath and sublimate was collected at reduced pressure on cold finger.

## Results and Discussion

The results of the spectrophotometric studies are summarized in Table 1 The copper complexes are bluish to purple in colour, but the bands in visible region are not sufficiently sensitive for practical analytical purposes. However the yellow colour of nickel complexes shows reasonable sensitivity, which obey Beer's law at their respective wavelengths of maximum absorbances.

The volatility of copper and nickel complexes was checked by sublimating the metal complexes at reduced pressure (0.5mm Hg) and sublimate was collected on a cold finger at 175-190°C.

Results of the TG and DTG analysis are summarized in Table 2 (Fig. 1&2), These indicate that the nickel (II) complexes of both *meso*-SD$A_2$ and DL-SD$A_2$ are completely volatile, the loss in weight is almost quantitative. However both the copper complexes are not sufficiently volatile and incomplete loss in weight occurs at high temperatures and leave 14-22% residue behind.

**Table 1.** Quantitative Absorptiometric Studies of Copper (II) and Nickel (II) Complexes.

| Compound | Metal ion | Solvent | $\lambda-$max nm | $\varepsilon$-mol$^{-1}_{cm}$ $-1$ | Solution Stability | Calibration range |
|---|---|---|---|---|---|---|
| *Bis*(acetylacetone) *meso*-stilbenediimine | Copper (II) | 1,2-dichloroethane | 650<br>560 | 144<br>162 | week | — |
| | Nickel (II) | Acetone | 560<br>357 | 135<br>7650 | week | Obeys Beer's law in the range of 16-48μg/ml of nickel complex. Corresponding to 2.16-4.48μg/ml of nickel at 357nm. |
| *Bis*-(acetylacetone)-DL-stilbenediimine | — | Chloroform | 310<br>243 | 24722<br>2256 | — | — |
| | Copper (II) | Chloroform | 540 | 198 | week | — |
| | Nickel (II) | Chloroform | 565<br>375 | 100<br>6518 | week | Obeys Beer's law over the range of 8-80μg/ml of complex corresponding to 1.08-10.85μg/ml of nickel at 375nm. |

**Table 2.** Thermogravimetry of Copper (II) and Nickel Complexes.

| Compound | Copper (II) Complex | Nickel (II) Complex |
|---|---|---|
| 1. *Bis*(acetylacetone) *meso*-stilbenediimine | Loss in weight starts at 243°C and loss of 78% by 439°C with black residue. | Loss in weight starts at 237 and loss of 100% 420°C. |
| 2. *Bis*(acetylacetone) DL-stilbenediimine | Brown Crystals,<br>Loss in weight starts at 195°C and loss of 80% by 320°C and further at 535°C to leave residue 14%. | Loss in weight starts at 240°C and loss of 99% 360°C. |

In view of the high temperatures needed for the volatilisation of the metal complexes, OV101, 3% on chromosorb (80-100mesh size), was considered to be a suitable liquid phase, followed by OV1, 3% on Uniport (80-100mesh size), packed in stainless steel columns 2m×3mm. The OV101, 3% on Chromosorb column gave satisfactory results. The operating temperatures were optimized. The most suitable column temperature for copper and nickel complexes of *meso*-$SDA_2$ was 255°C and for DL-$SDA_2$ 250°C.The injection temperature was fixed at 280°C in all cases. The optimum flow rate of nitrogen was 22ml/min. The retention times are summarized in Table 3 and typical chromatograms are shown in Fig. 4&5. Nickel complexes of *meso*-$SDA_2$ and DL-$SDA_2$ show symmetrical peaks with a stable base line. However the corresponding copper complexes particularly *meso*-$SDA_2$ show slight base line drift probably due to partial decomposition of the complexes.

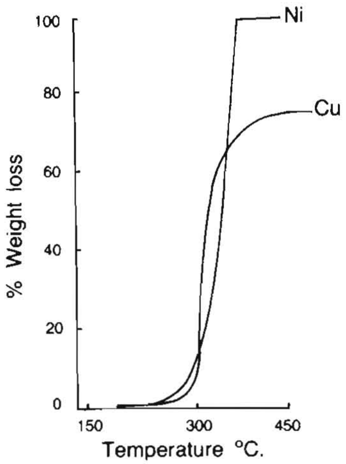

**Fig. 1.** Thermograms of Copper(II) and Nickel Chelates of *Bis* (acetylacetone) *meso*-stilbehediimine.

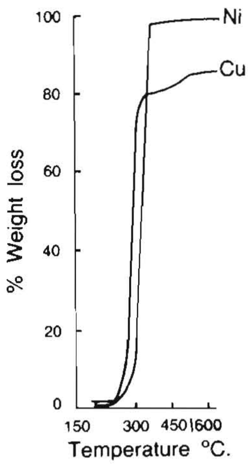

**Fig. 2.** Thermograms of Copper(II) and Nickel(II) Chelates of *Bis*(acetylacetone)DL-stilbenediimine.

**Table 3.** Retention Time in Seconds.

| | **Reagent** | **Copper Complex** | **Nickel Complex** |
|---|---|---|---|
| *Bis*(acetylacetone)-*meso*-stilbenediimine | 325 | 768 | 828 |
| *Bis*(acetylacetone)-DL-stilbenediimine | 330 | 624 | 672 |
| *Bis*(acetylacetone) ethylenediimine | 160 | 408 | 556 |

When a mixture of copper and nickel chelates of DL-$SDA_2$ and *meso*-$SDA_2$ was injected on column temperature of 250°C, complete separation of metal complexes of DL and *meso*-geometrical isomers was achieved, but an attempt to resolve racemic product under present conditions proved unsuccessful. The copper and nickel complexes of DL-$SDA_2$ and *meso*-$SDA_2$ were only partially resolved.

To check if the response of the detection was linear with the amount injected, solutions of known amount of the complexes in acetone were injected and the peak area (hight into width at half height) of at least two injections were measured. Linear calibration curves were obtained in the range of 0.4-6.0µg and 2-9µg of complexes for *meso*-$SDA_2$ Ni and *meso*-$SDA_2$ Cu respectively, corresponding to 0.05-0.81µg nickel and 0.3-1.3µg of copper with average relative deviations within ± 2.5% (six replicates) (Fig. 3). Practical limits of detection of *meso*-$SDA_2Ni$ and *meso*-$SDA_2Cu$ were found 0.1µg and 0.5µg respectively, corresponding to 13ng nickel and 72ng copper.

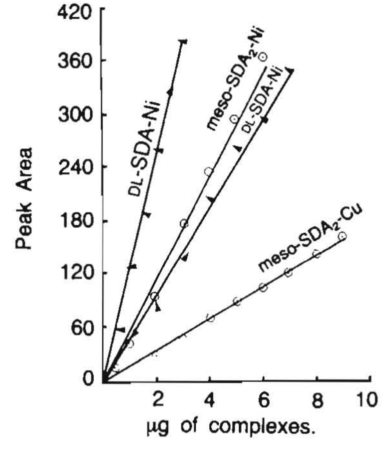

**Fig. 3.** Calibration cruves of Copper and Nickel complexes of *bis*(acetylacetone)DL-stilbenediimine and *bis* (acetylacetone)*meso*-stilbenediimine.

Similarly the linear calibration ranges for DL-$SDA_2Ni$ and DL-$SDA_2Cu$ were found 0.5-3.0μg and 1.0-7.0μg respectively, corresponding to 0.07-0.47μg nickel and 0.14-1.0μg of copper with relative average deviation within ± 2% (Seven replicates). Practical limits of detection of DL-$SDA_2Ni$ and DL-$SDA_2Cu$, at least twice the base line signal were found 0.05μg and 0.2μg respectively, corresponding to 6ng of nickel and 29ng of copper.

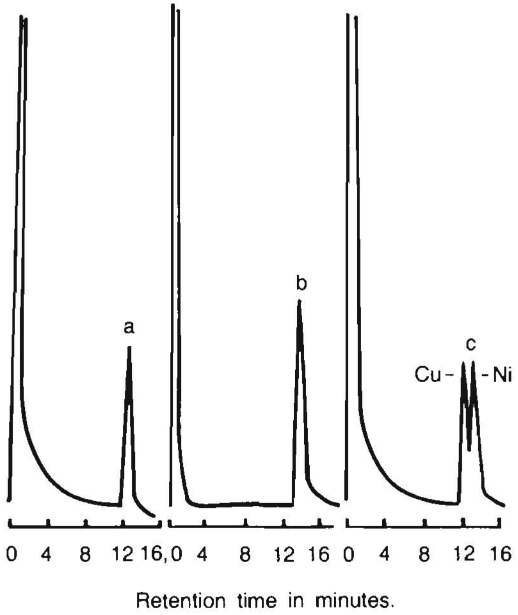

**Fig. 4.** Relative Gas Chromatographic responses (a) 6.0μg of *meso*-$SDA_2Cu$ (b) 2.0μg of *meso*-$SDA_2Ni$ (c) Mixture of 5.3μg of *meso*-$SDA_2Cu$ and 1.3μg of *meso*-$SDA_2Ni$. 2m x 3mm stainless steel column at 255°C. Stationary phase OV101, 3% on chromosorb WHP 80-100 mesh size. Nitrogen flow rate $22cm^3$/min.

The calibration data shown in Fig. 4 indicates that *meso*-$SDA_2Cu$ complex is least sensitive in the series, due to distortion from the square planner configuration of the complex as a result of steric hinderance between the methyl and the equatorial phenyl groups (Kanatomi *et al.* 1976). This could be responsible for the decomposition of the complex, as indicated by TG curve with 22% nonvolatile residue and the adsorption of the complex on the column. However such steric hinderance does not exist in DL-$SDA_2$ due to diaxial conformation of phenyl groups and the complexes showed better sensitivity.

In order to compare the gas chromatographic responses of copper and nickel complexes of DL-$SDA_2$ and *meso*-$SDA_2$ with that of *bis*-(acetylacetone) ethylenediimine ($enA_2$), the $enA_2Cu$ and $enA_2Ni$ complexes were chromotographed on 2mx3mm stainless steel column packed with OV101, 3% on chromsorb (80-100mesh size) at a column temperature of 220°C and injection temperature of 270°C with a nitrogen flow rate of $22cm^3$/min. The retention times are shown in Table 3 and their relative responses in Fig. 6. Practical limits of detection of copper and nickel chelates of $enA_2$ were found to be 0.4μg and 0.2μg respectively corresponding to 89ng of copper and 41ng of nickel.

Therefore the results indicate that the addition of bulky phenyl groups at the bridge position particularly in DL-isomer improves the sensitivity and the detection limit of the metal ions considerably.

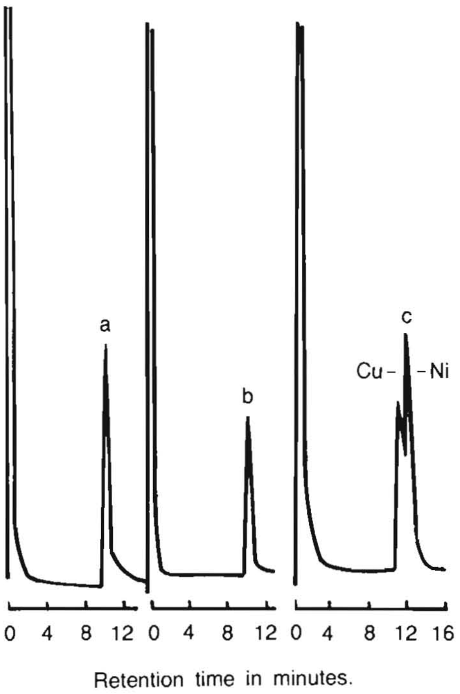

**Fig. 5.** Relative Gas Chromatographic Responses (a) 4.0μg of DL-$SDA_2Cu$ (b) 1.0μg of DL-$SDA_2Ni$ (c) Mixture of 3.0μg of DL-$SDA_2Cu$ and 1.5μg of DL-$SDA_2Ni$.
2m x 3mm Stainless steel column at 250°C. Stationary phase, 3% OV101 on Chromosorb WHP 80-100 mesh size. Nitrogen flow rate 22 $cm^3$/min.

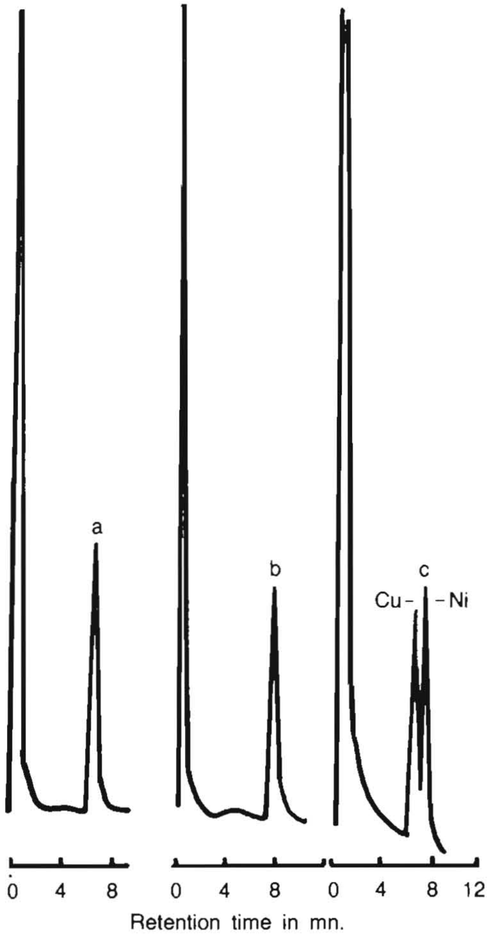

**Fig. 6.** Relative Gas Chromatographic Responses (a) 4.µg of en $A_2$ Cu (b) 2.0µg of en$A_2$Ni (c) Mixture of 4.0µg of en$A_2$Cu and 2.0µg of en$A_2$Ni.
2m x 3mm stainless steel column at 220°C. Stationary phase OV101, 3% on chromosorb WHP 80-100 mesh size Nitrogen flow rate 22 $cm^3$/min.

## Conclusion

The work examplifies the potentials of the reagents for the determination of metal ions at ng levels with the aid of GLC equipped with flame ionization detector. The nickel complexes are more sensitive spectrophotometrically, more volatile and show higher sensitivity with lower detection limit gas chromatographically than the corresponding copper complexes. Moreover copper and nickel complexes of DL-$SDA_2$ show better sensitivity with lower detection limits than corresponding copper and nickel complexes of *meso*-$SDA_2$ gas chromatographically. A mixture of metal complexes of DL and *meso*-geometrical isomers can easily be separated, but a mixtures of copper and nickel complexes are only partially resolved. The gas chromatographic responses of the metal complexes prepared and developed in the present investigation were compared with the corresponding metal complexes of the well known *bis*(acetylacetone) ethylenediimine reagent. The results show that copper and nickel complexes of the reagent particularly DL-$SDA_2$ are more sensitive with better detection limit that $enA_2$ probably due to phenyl group substitution at bridge position.

## *Acknowledgement*

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# بعض الدراسات القياسية الجذبية الحرارية والرسمية اللونية الغازية لمركبات الحديد (II) والنيكل (II) للميزو وال D.L و D.L ـ بس (استيل استون) ستل بندمين

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المركز الوطني المتقدم للكيمياء التحليلية
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يكون كل من الـ بس (استيل استون) ميزو ـ ستل بندمين والـ بس (استيل استون) D.L ـ ستل بندمين كلّابيات (Chelares) ملونة للنحاس (II) والنيكل (II). إن مركبات النحاس (II) غير حساسة للقياس الرسمي الطيفي، إلا أن مركبات النيكل أظهرت حساسية معقولة له. وبالتماثل فإن الدراسات TG وDTG تشير إلى أن مركبات النيكل نسبياً أكثر تطايراً وحرارياً مستقرة، إذا ما قورنت بالنسبة لكلابيان النحاس.

المركبات المعدنية يمكن رسمها بسهولة لونياً غازياً من 0V-101 و ٣٪ على عمود ماص الألوان (٨٠ ـ ١٠٠ شبكة حجماً). إن مدى المعايرة وحدود الكشف وميز مركبات النحاس والنيكل قد ثبتت في هذا البحث. كما أن مركبات النيكل أظهرت أيضاً حساسية أعلى، تجاه الحد الأدنى للكشف عند مستويات النانوجرام (ng)، من مثيلاتها مركبات النحاس.