nitudes of the intensities for $\mathrm{Ni(napy)_2(NO_3)_2}$ lie between those of $\mathrm{Ni(NO_3)_4^{2-}}$ and $\mathrm{Ni(napy)_4^{2+}}$.

The single band observed in the solid spectrum of $\mathrm{Cu(napy)_2(NO_3)_2}$ undergoes a shift to greater wavelength when the complex is placed in solution. This shift may result from a change in coordination similar to that observed for $\mathrm{Fe(napy)_4^{2+}}$.[7,8b,38] Such behavior could be indicative of the breaking of bridging nitrates which are proposed for the solid state on the basis of solubility and infrared combination bands. The position of the band and the magnitude of ϵ_{max} occur between those observed for $\mathrm{Cu(NO_3)_4^{2-}}$ [28] and $\mathrm{Cu(napy)_4^{2+}}$.[8b]

The pmr spectrum of $\mathrm{Zn(napy)_2(NO_3)_2}$ in nitromethane shows the following chemical shifts (δ) for the 2,7, 4,5, and 3,6 protons, respectively, with line widths at half-height in parentheses: $\mathrm{Zn(napy)_2(NO_3)_2}$, 9.14 (8), 8.63 (14), 7.81 (12); napy, 9.05 (8), 8.35 (14), 7.56 (12). Monosubstitution of napy results in measurable differences in chemical shift for the now nonequivalent 2 and 7 protons and the 4 and 5 protons.[39,40] The sharp resonance pattern for the Zn complex in which the peaks have not undergone any broadening suggests bidentate coordination of napy. Electron donation from napy to the metal ion is indicated by the deshielding of the napy protons upon coordination. The Cd complex was not sufficiently soluble to obtain a satisfactory pmr spectrum.

Registry No. Manganese nitrate hexahydrate, 17141-63-8; cobalt nitrate hexahydrate, 10026-22-9; nickel nitrate hexahydrate, 13478-00-7; copper nitrate trihydrate, 10031-43-3; zinc nitrate hexahydrate, 10196-18-6; cadmium nitrate tetrahydrate, 10022-68-1; $\mathrm{Mn(napy)_2(NO_3)_2}$, 37475-80-2; $\mathrm{Co(napy)_2(NO_3)_2}$, 37454-25-4; $\mathrm{Ni(napy)_2(NO_3)_2}$, 37189-82-5; $\mathrm{Cu(napy)_2(NO_3)_2}$, 37189-81-4; $\mathrm{Zn(napy)_2(NO_3)_2}$, 37454-26-5; $\mathrm{Cd(napy)_2(NO_3)_2}$, 37454-24-3.

Acknowledgments. We gratefully acknowledge the support of this work by the Research Corp. in the form of a Frederick Gardner Cottrell grant. We also wish to thank Dr. Devon Meek of The Ohio State University for the use of the Faraday apparatus.

---

(38) E. Dittmar, C. J. Alexander, and M. L. Good, *J. Coord. Chem.*, 2, 69 (1972).

(39) W. W. Paudler and T. J. Kress, *J. Heterocycl. Chem.*, 5, 561 (1968).

(40) D. J. Pokorny, Ph.D. Dissertation, Ohio University, 1972.

Contribution from the Department of Chemistry,
University of Massachusetts, Amherst, Massachusetts 01002

Resolution of Volatile *N,N'*-2,3-Butylenebis(trifluoroacetylacetoniminato)copper(II), -nickel(II), and -palladium(II) Chelates by Gas-Liquid Chromatography

P. C. UDEN* and K. BLESSEL

Received July 5, 1972

N,N'-2,3-Butylenebis(trifluoroacetylacetoniminato) chelates of copper(II), nickel(II), and palladium(II) each exhibit two isomeric forms which can be readily resolved by gas-liquid chromatography. These chelates and their analogs are sufficiently volatile and thermally stable for quantitative elution with no evidence of decomposition or other adverse column interactions. The meso and racemic forms of the Cu(II) chelates are prepared in a high state of purity by fractional recrystallization of 2,3-butylenediamine hydrochloride followed by reaction with trifluoroacetylacetone and complex formation. Thermogravimetry, elemental analysis, and mass spectrometry are employed to confirm the identity and purity of the chelates. Interfaced mass spectrometry is also used to confirm the identity of the eluted gas chromatographic peaks.

Introduction

Analytical procedures for the determination of metals as volatile neutral monomeric chelates using the methods of gas-liquid chromatography, thermogravimetry, and mass spectrometry are now well established, particularly for complexes of the type $\mathrm{M^{III}(\beta\text{-dik})_3}$[1-6] (dik = diketonate) and to a limited extent $\mathrm{M^{II}(\beta\text{-dik})_2}$,[7-9] most attention being paid to chromium and beryllium β-diketonates.

In contrast, few studies by gas chromatography of the chemical nature and reactivity of metal complexes have been performed. The resolution of the geometrical isomers of the chromium chelates of unsymmetrical β-diketonates such as trifluoroacetylacetone has been accomplished on moderately polar gas chromatographic stationary phases,[10] the separation indeed paralleling that claimed by adsorption chromatography.[11] Some success has also been achieved in the resolutions of *d* and *l* isomers of octahedral complexes such as chromium hexafluoroacetylacetonate by utilizing interactions with optically active substrates.[12] Redistribution reactions of different β-diketonate ligand moieties on metals have also

---

(1) R. W. Moshier and R. E. Sievers, "Gas Chromatography of Metal Chelates," Pergamon Press, Oxford, 1965.

(2) J. L. Booker, T. L. Isenhour, and R. E. Sievers, *Anal. Chem.*, 41, 1705 (1969).

(3) W. D. Ross and R. E. Sievers, *Anal. Chem.*, 41, 1109 (1969).

(4) J. Savory, P. Mushak, and F. W. Sunderman, Jr., *J. Chromatogr. Sci.*, 7, 674 (1969).

(5) N. M. Frew, J. J. Leary, and T. L. Isenhour, *Anal. Chem.*, 44, 665 (1972).

(6) R. Belcher, C. R. Jenkins, W. I. Stephen, and P. C. Uden, *Talanta*, 17, 455 (1970).

(7) W. D. Ross, *Talanta*, 15, 87 (1968).

(8) J. K. Foreman, T. A. Gough, and E. A. Walker, *Analyst (London)*, 95, 797 (1970).

(9) R. Belcher, J. R. Majer, W. I. Stephen, I. J. Thomson, and P. C. Uden, *Anal. Chim. Acta*, 50, 423 (1970).

(10) R. E. Sievers, B. W. Ponder, M. L. Morris, and R. W. Moshier, *Inorg. Chem.*, 2, 693 (1963).

(11) R. C. Fay and T. S. Piper, *J. Amer. Chem. Soc.*, 85, 500 (1963).

(12) R. E. Sievers, R. W. Moshier, and M. L. Morris, *Inorg. Chem.*, 1, 966 (1962).

been briefly described using gas chromatography to monitor the reactions.[13]

The relative lack of application of this powerful technique to metal chelate studies may be attributable, at least in part, to the relative instability or reactivity of many β-diketonate chelates. In particular in the case of divalent transition metal ions having coordination numbers greater than 4, the neutral chelate molecule may act as a Lewis acid, forming stable base adducts, the presence of which precludes ready volatilization.[14,15] Dimeric and trimeric forms also frequently occur.

We have recently reported gas chromatography of metal complexes of thio derivatives of β-diketones, and the potential applicability for studies involving divalent transition metal chelates appears to be considerable.[16,17] Miyazaki, *et al.*, studied the gas chromatographic characteristics of Cu(II) and Ni(II) chelates of salicylaldimines and β-keto imine derivatives of acetylacetone, only bis(4-aminopent-3-ene-2-ono)nickel(II) showing sufficient stability for quantitative chromatography.[18] We have reported the gas chromatography of *N,N'*-alkenebis(β-keto iminato) complexes of Cu(II), Ni(II), Pd(II), and Pt(II), which exhibit thermal stability to above 300° and quantitative chromatographic elution to the nanogram level.[19,20] In the course of these studies we have observed that for the Cu(II), Ni(II), and Pd(II) chelates of *N,N'*-2,3-butylenebis(trifluoroacetylacetonimine) two distinct gas chromatographic peaks are always observed for each complex.

In this paper we show that for the Cu(II) complex the two resolved components are attributable to different forms of the diamine bridge; evidence is strong that the nickel and palladium chelates behave similarly.

Experimental Section

2,3-Butylenediamine (2,3-Diaminobutane). The diamine was prepared by the method of Dickey, *et al.*[21] Samples were also obtained from Wyandotte Chemical Corp. The meso and racemic isomers were partially separated by fractional recrystallization of the amine hydrochlorides from aqueous methanol,[21] the relative amounts of each isomer being estimated from nmr spectra using the procedure of Sudmeier and Reilly.[22] Three successive recrystallizations produced a product which contained greater than 90% of the meso diamine from a starting material whose isomer ratio was approximately 1:1. The highest enrichment of the racemic form which could be readily obtained by this procedure was about 2:1 and further separation of the chelates was eventually needed. These various forms of the diamine hydrochloride were reconverted to free diamine by treatment of aqueous solutions with potassium hydroxide followed by extraction into diethyl ether.

***N,N'*-2,3-Butylenebis(trifluoroacetylacetonimine) [$H_2bn(TFA)_2$].** This was prepared by the reaction of stoichiometric quantities of the appropriate 2,3-butylenediamine isomer mixtures with trifluoroacetylacetone (Columbia Organic Chemicals, Inc.), each in 10% ethanolic solution, the optimal yields being obtained by warming to 60° for *ca.* 20 min. The product was precipitated from solution by the addition of diethyl ether and recrystallized from that solvent. *Anal.* Calcd: C, 46.65; H, 5.04; N, 7.78. Found: C, 46.68; H, 5.07; N, 7.67 (for ligand prepared from approximately 1:1 meso:racemic diamine); C, 46.85; H, 5.08; N, 7.70 (for ligand prepared from approximately 9:1 meso:racemic mixture).

$Cu(bn(TFA)_2)$. The chelate was prepared by two methods: (i) refluxing an acetone solution of the ligand over anhydrous cupric hydroxide, followed by filtration, evaporation, and recrystallization of the product from aqueous methanol; (ii) addition of an acetone solution of the ligand to aqueous ammoniacal cupric nitrate and extracting the chelate so formed into chloroform. *Anal.* Calcd: C, 39.84; H, 3.83; N, 6.64. Found (for 1:1 meso:racemic ligand): C, 39.86; H, 3.85; N, 6.66. The chelate so prepared gave a blue solution in organic solvents from which both purple and greenish crystals were evident on evaporation.

$Cu(bn(TFA)_2)$ (Meso). The meso form of the chelate (as subsequently proven) was prepared by the cupric hydroxide method from the ligand made from 9:1 meso:racemic diamine. A single recrystallization of this complex from aqueous methanol gave a dark green crystalline compound subsequently shown to be almost completely free of the racemic isomer. *Anal.* Found: C, 39.75; H, 3.80; N, 6.79.

$Cu(bn(TFA)_2)$ (Racemic). Since the highest proportion of racemic $H_2(bn(TFA)_2)$ which could readily be obtained was approximately 60% (as shown both from the nmr of the starting butylenediamine and by gas chromatography of the prepared copper chelate) and since recrystallization procedures proved ineffective in removing the meso isomer completely, adsorption column chromatography was employed to isolate the racemic copper complex. Optimal resolution was obtained with a silica gel column (activity grade, approximately 2.5 on the Brockman scale) using 70:30 benzene–hexane as eluent. Samples of the mixture of up to 250 mg were partially separated into a purple band (eluting first) and a blue-green band. Repeated chromatography finally gave a sample having greater than 99% of the purple racemic form. *Anal.* Found: C, 39.74; M, 3.89; N, 6.60.

$Ni(bn(TFA)_2)$. The chelate was prepared by refluxing an acetone solution of the ligand over anhydrous nickel hydroxide, followed by filtration, evaporation, and precipitation of the crystalline complex by addition of water to an acetone solution. After drying at 100° under vacuum, gas chromatography showed a ratio of two peak areas again corresponding to the racemic and meso forms of approximately 5:1 (*cf.* approximately 1:1 for the copper complex). It was noted that the meso form (the second smaller component) appeared to form more slowly, the above ratio being the lowest noted. *Anal.* Calcd: C, 40.30; H, 3.87; N, 6.72. Found: C, 40.21; H, 3.92; N, 6.80.

$Ni(bn(TFA)_2)$ (Racemic). Recrystallization of the complex from aqueous methanol produced a sample shown by gc to contain less than 0.1% of the meso form (second peak). *Anal.* Found: C, 40.28; H, 3.90; N, 6.63.

$Ni(bn(TFA)_2)$ (Meso). The meso form of the complex was not isolated in a pure state. Silica gel column chromatography did not achieve adequate separation from the racemic form which was always the major component in any fraction taken. Also, the reaction of the 90% meso form of the ligand with nickel hydroxide gave too small a yield of the chelate to be isolated even after prolonged reflux.

$Pd(bn(TFA)_2)$. The chelate was prepared by refluxing excess ligand with a benzene solution of $PdCl_2 \cdot 2C_6H_5CN$ followed by filtration, evaporation, and recrystallization from chloroform. *Anal.* Calcd: C, 36.18; H, 3.47; N, 6.03. Found: C, 36.28; H, 3.53; N, 6.10. Meso and racemic forms were not isolated.

Gas Chromatography. A Perkin–Elmer 990 gas chromatograph was used, employing flame ionization detection. Various columns (2 m; $^1/_8$-in. o.d.; stainless steel) packed with Apiezon L, SE30 silicone gum rubber, or QF 1 (fluoropropyl silicone oil) on Anakrom ABS support all gave complete resolution of the two forms of each complex. Generally solutions of concentration around 1 mg/ml were prepared in acetone and 1-μl samples were analyzed. Peak area integration was accomplished with a Vidar Autolab 6300 electronic integrator. The relative areas of the gas chromatographic peaks for two isomers of the *N,N'*-2,3-butylenebis(trifluoroacetylacetoniminato) chelates as obtained by digital integration may be expected to give good values for the true relative proportions of the components. The responses of the flame ionization detector to the two isomers will be identical, and since the detector is mass-flow sensitive, the integrated peak areas of equal quantities of two identically responsive components having different retention times will be identical.

Mass Spectrometry. Mass Spectra of the ligands and chelates were obtained on a Hitachi Perkin–Elmer RMU.6L single focusing mass spectrometer operating at an ionizing voltage of 80 eV. The source temperature was maintained at 210 ± 5° and solid samples

---

(13) R. Linck and R. E. Sievers, Abstracts, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1964, p 52.

(14) J. P. Fackler, Jr., *Progr. Inorg. Chem.*, 7, 361 (1966).

(15) D. F. Graddon, *Coord. Chem. Rev.*, 4, 1 (1969).

(16) R. Belcher, W. I. Stephen, I. J. Thomson, and P. C. Uden, *J. Inorg. Nucl. Chem.*, 33, 1851 (1971).

(17) R. Belcher, W. I. Stephen, I. J. Thomson, and P. C. Uden, *J. Inorg. Nucl. Chem.*, 34, 1017 (1972).

(18) M. Miyazaki, T. Imanari, T. Kunugi, and Z. Tamura, *Chem. Pharm. Bull.*, 14, 117 (1966).

(19) R. Belcher, M. Pravica, W. I. Stephen, and P. C. Uden, *Chem. Commun.*, 41 (1971).

(20) R. Belcher, K. Blessel, T. J. Cardwell, M. Pravica, W. I. Stephen, and P. C. Uden, *J. Inorg. Nucl. Chem.*, submitted for publication.

(21) F. H. Dickey, W. Fickett, and S. Lucas, *J. Amer. Chem. Soc.*, 74, 944 (1952).

(22) J. L. Sudmeier and C. N. Reilley, *Anal. Chem.*, 36, 1707 (1964).

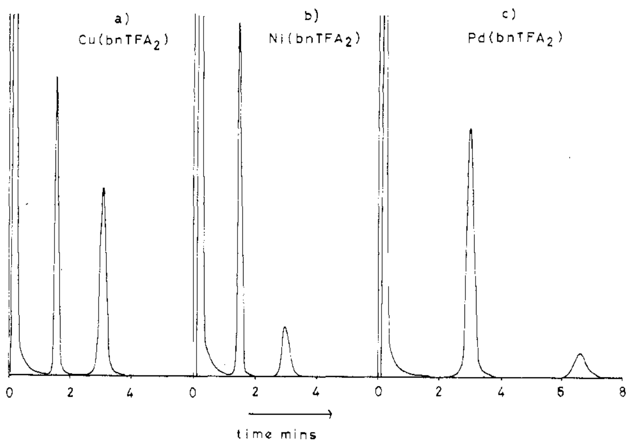


Figure 1. Chromatograms of copper(II), nickel(II), and palladium(II) *N,N'*-2,3-butylenebis(trifluoroacetylacetoniminato) chelates. Column 6 ft × $^1/_8$ in. o.d. stainless steel packed with 5% Apiezon L on Anakrom ABS, 90–100 mesh; helium flow rate 50 cm^3 min^{-1}; column temperature 250°; injector and flame ionization detector temperatures 260°. Solutions 1 mg ml^{-1} in chloroform; 1-μl samples.

were evaporated into the source with the direct insertion probe. Two different gc–ms interface systems also gave virtually identical results for spectra obtained from gc peaks: a Perkin-Elmer 900 gas chromatograph interfaced with a Hitachi RMS.4 using a jet separator and a Perkin-Elmer 990 interfaced with the Hitachi RMU.6L using a Watson–Biemann separator. The interfaces were generally operated at temperatures 30–50° above the column temperature.

Thermal Analysis. Thermogravimetric curves were recorded on a Du Pont 950 thermogravimetric analyzer, using *ca.* 2-mg samples and a heating rate of 5°/min. Helium purge gas was employed at a flow rate of 60 cm^3 min^{-1}.

Nmr. Spectra of the diamine hydrochloride were taken on Varian A-60 and Perkin-Elmer R 12A spectrometers with acetic acid as an internal standard in deuterium oxide solution.

Elemental Analyses. Carbon, hydrogen, and nitrogen determinations were made in the microanalytical laboratory of the University of Massachusetts.

Results and Discussion

N,N'-2,3-Butylenebis(β-keto iminato) chelates are of interest from a number of viewpoints. First, it is predictable that they will be more volatile and thermally stable than the analogous propylene complexes since these are in turn more stable and volatile than the ethylene derivatives.[19,20] Thus gas chromatographic applicability would be enhanced.

Second, 2,3-butylenediamine exists in both meso and racemic forms,[23] each form showing the possibility of $\delta \rightleftharpoons \lambda$ conversion. In the case of simple complexation of the diamines themselves with a metal ion, the meso isomer will have one methyl group in an axial environment and one methyl group in an equatorial environment while the optically active isomer has both methyl groups in similar environments. It might be predicted that these configurations would persist on condensation of the diamine with two molecules of trifluoroacetylacetone to produce two isomeric forms of *N,N'*-2,3-butylenebis(trifluoroacetylacetonimine) [$H_2(bn(TFA)_2)$] and that these meso and racemic forms would retain their identity on complexation with divalent transition metal ions.

Figure 1 shows two well-resolved chromatographic peaks for analytically pure complexes of Cu(II), Ni(II), and Pd(II) as prepared from the ligand having an approximately 1:1 racemic:meso ratio. The ratio of areas for the chelates are typically 1:1, 5:1, and 7:1, respectively. The two peaks appear for complexes produced both from the diamine as obtained commercially and from that prepared by the reduction of dimethylglyoxime. In the case of the copper and nickel chelates observation of the flame color in the flame ionization detector verifies that both peaks observed for each complex correspond to eluents containing the appropriate metals.

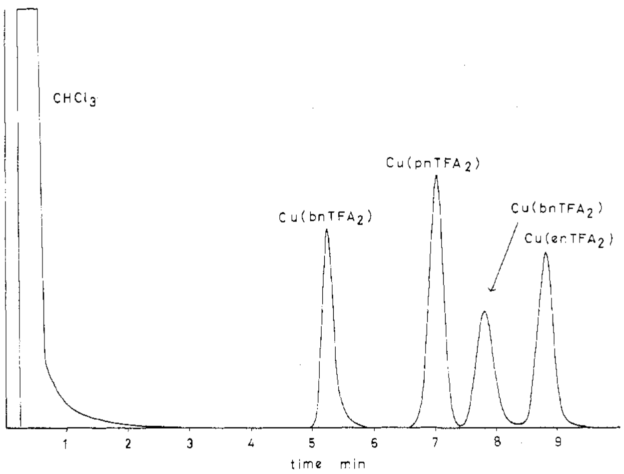


Figure 2. Chromatogram of bridged (keto amine)copper(II) chelates. Column 5 ft × $^1/_8$ in. o.d. stainless steel packed with 3% QF.1 fluorosilicone oil on Varaport 30, 100–110 mesh; helium flow rate 50 cm^3 min^{-1}; column temperature 210°; injector and flame ionization detector temperatures 250°. Each complex 1 mg ml^{-1} in chloroform solution; 1-μl samples.

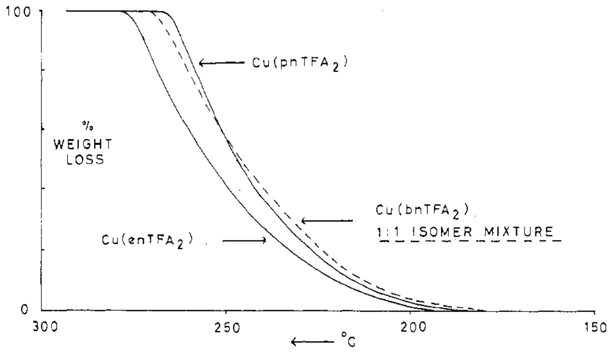


Figure 3. Thermograms of bridged (keto amine)copper(II) chelates; 2-mg samples, heating rate 5°/min.

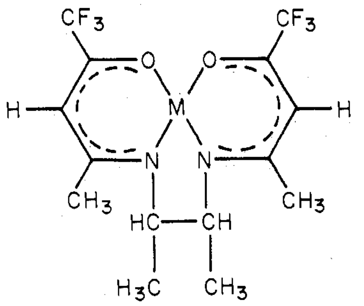
Gas chromatography of a mixture of $Cu(bn(TFA)_2)$ and its ethylene- and propylenediamine analogs, $Cu(en(TFA)_2)$ and $Cu(pn(TFA)_2)$ (Figure 2), indicates that the first eluted component for $Cu(bn(TFA)_2)$ appears in a position as predicted for a complex having enhanced volatility produced on substituting methyl groups on the bridging carbons but the second component has much lower volatility than predicted. These chromatographic characteristics persist over a sample size range from 100 μg to 1 ng, indicating linear sample response for each component over this range with no losses on the column resulting from adsorption or decomposition.

Further indication that the $Cu(bn(TFA)_2)$ complex consists of two species is evident from a thermogram (Figure 3); while complete volatilization occurs for all the chelates, the $Cu(bn(TFA)_2)$ complex begins to volatilize at a lower temperature than either the $Cu(pn(TFA)_2)$ or the $Cu(en(TFA)_2)$ complexes but the trace intersects the former at around 50% weight loss and the residual complex then volatilizes at a higher temperature than $Cu(pn(TFA)_2)$. These data, in addition to the values obtained for the carbon, hydrogen, and nitrogen contents of the copper and nickel complexes which confirm stoichiometry, clearly indicate the presence of two

---

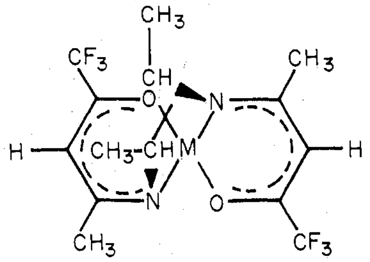
(23) R. F. Evilia, D. C. Young, and C. N. Reilley, *Inorg. Chem.*, 10, 433 (1971).

gas chromatographically resolvable isomers. Structure I is



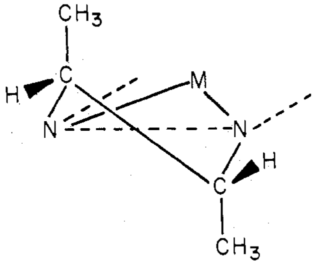
I

the only acceptable ligand orientation with respect to trifluoromethyl groups since the condensation of primary amines with trifluoroacetylacetone is known to proceed entirely through the carbonyl group adjacent to the methyl group,[24-27] and an alternative structure of the type II may be excluded on steric grounds for a planar metal complex.

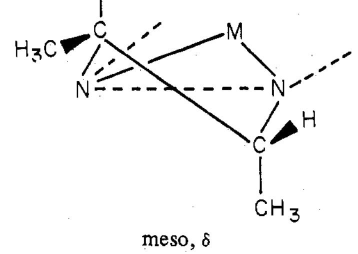


II

The orientation of the bridging group methyl substituents remains the sole plausible explanation for the observed isomeric forms (III and IV).



d, γ
III



meso, δ
IV

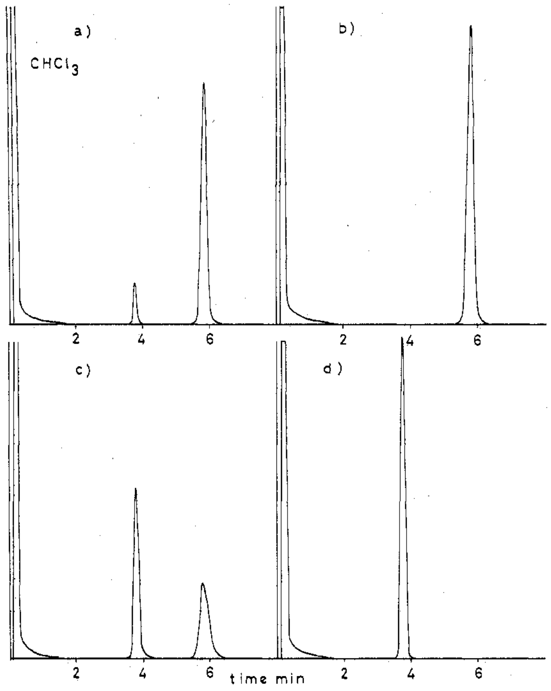


Figure 4. Chromatograms of $Cu(bn(TFA)_2)$ isomers. Column and conditions as in Figure 2 except column temperature is 215°: (a) sample prepared from 9:1 meso:racemic diamine; (b) sample a after recrystallization from aqueous methanol; (c) sample prepared from 4:6 meso:racemic diamine; (d) sample (first purple fraction) separated by silica gel column chromatography.

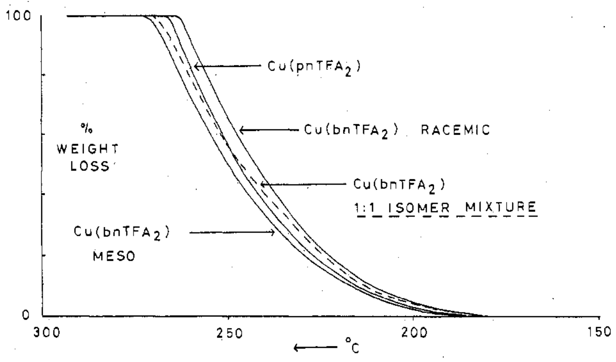


Figure 5. Thermograms of $Cu(bn(TFA)_2)$ isomers; 2-mg samples, heating rate 5°/min.

The copper complexes were chosen for a more complete investigation to substantiate this hypothesis, purple and blue-green forms being isolated as noted previously, these forms corresponding to the first and second gas chromatographic peaks, respectively.

Figure 4a shows the gas chromatogram of $Cu(bn(TFA)_2)$ as prepared from the ligand made from 9:1 meso:racemic diamine, while Figure 4b shows the peak ratio after recrystallization from aqueous methanol to give dark green crystals. Figure 4c shows the same complex prepared from the 4:6 meso:racemic diamine and Figure 4d shows the purple chelate obtained from repeated silica gel column chromatography (collection of early fractions eluted in each column run).

Figure 5 shows thermograms of the purple and green forms of $Cu(bn(TFA)_2)$ under the same conditions as in Figure 3, again in comparison with the analogous ethylenediamine and propylenediamine complexes ($Cu(en(TFA)_2)$ and $Cu(pn(TFA)_2)$). It is again clear that the purple isomer is more volatile than the $Cu(pn(TFA)_2)$ while the green isomer is less volatile.

---

(24) P. J. McCarthy and A. E. Martell, *J. Amer. Chem. Soc.*, 78, 2106 (1956).

(25) R. J. Hovey and A. E. Martell, *J. Amer. Chem. Soc.*, 82, 364 (1960).

(26) R. J. Hovey and A. E. Martell, *J. Amer. Chem. Soc.*, 82, 2697 (1960).

(27) P. J. McCarthy and A. E. Martell, *J. Amer. Chem. Soc.*, 78, 264 (1956).

Further evidence was obtained by observation of their mass spectra. Three solid samples were analyzed using the direct solids probe, the 1:1 mixture, and the purified purple and green complexes. Identical spectra were obtained, the major features of the spectrum together with assigned fragments being given in Figure 6, leaving no doubt as to the identity of the chelates. The fragmentation pattern observed is a very simple one, copper-containing fragments being readily distinguished by the presence of the ^{63}Cu-^{65}Cu isomer pair. The major fragment ion corresponds to a symmetrical cleavage of the diamine bridge of the ligand, half of the ligand remaining bonded to copper (*m/e* 242; relative intensity 100). By comparison the molecular ion has a relative intensity of 35. It is significant that no free ligand fragment is observed (in contrast with the fragmentation of bidentate β-diketonate chelates), thus emphasizing the stability of the tetradentate chelate structure. Relatively low intensity fragments are also observed corresponding to the loss from the molecular ion of CH_3, F, 2 CH_3, and CF_3. These parallel closely those seen for other chelates of this series.[20] Spectra were also obtained directly from the two peaks eluted from the gas chromatographic column under standard conditions. Spectra obtained for two different instruments using different interfaces and molecular separator systems again gave identical definitive spectra for Cu(bn(TFA)$_2$) for both peaks.

While there are gas chromatographic precedents for attributing the first peak eluted in a meso–racemic isomer pair to be the meso form and the second to be the racemic form,[28] in the present case the weight of evidence clearly indicates the opposite assignment. The fractional crystallization method employed for resolution of the meso and racemic forms of the diamine as confirmed by nmr is well established and all evidence indicates that the meso or racemic configuration of the diamine bridge persists unchanged through formation of both the *N,N'*-2,3-butylenebis(trifluoroacetylacetonimine) ligand and the copper complexes.

The evidence that precisely the same situation holds for the nickel chelates is also very strong. The gas chromatographic retention data of the two peaks due to Ni(bn(TFA)$_2$) are closely similar to those for Cu(bn(TFA)$_2$), and in fact on nonpolar substrates such as Apiezon L retention times for the analogous copper and nickel peaks are within 1% of each other making resolution impossible. The coincidence of an exact retention time reversal of the two isomers is virtually impossible, particularly as the same behavior is observed on a number of stationary phases. The smaller amount of the meso nickel isomer formed from the 1:1 meso:racemic chelate as compared with the racemic isomer (1:5 at best) is again a factor seen in the difficulty observed in attempting to prepare the pure meso species from the 9:1 meso:racemic ligand. While no extensive studies were carried out for the palladium complexes, it is probable that similar conclusions may be drawn in this case also.

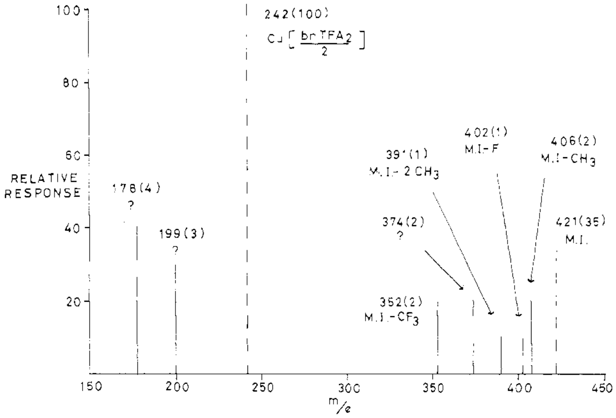


Figure 6. Bar-graph mass spectrum of Cu(bn(TFA)$_2$) (^{63}Cu shown). Direct solid probe mass spectrum of Cu(bn(TFA)$_2$), both isomers. Typical condition for spectral scan (RMU.6L) of eluent chromatographic peak. Column 6 ft × $^1/_8$ in. o.d. stainless steel packed with 7.5% OV.1 on Anakrom ABS, 90–100 mesh; helium flow rate 40 cm^3 min^{-1}; column temperature 240°; manifold and detector 280°; interface 290°; ion chamber 210°; pressure 2 × 10^{-6} Torr; accelerating voltage 80 eV. (*m/e* values denoted by – – – are present at ×10 intensity.)

From our study it is clear that the two gas chromatographic peaks obtained for the Cu, Ni, and Pd chelates correspond to meso and racemic forms of the diamine bridge, gas chromatography proving to be a powerful technique for the study of such systems. Further structural and spectral studies are also under way or are currently projected in this area; in particular it is hoped that X-ray crystallographic data may give some insight into the clear structural difference between the two chelate isomers resulting in particular in their marked volatility difference.

Registry No. H_2bn(TFA)$_2$, 37478-06-1; *meso*-Cu[bn(TFA)$_2$], 34478-07-2; (±)-Cu[bn(TFA)$_2$], 37478-08-3; (±)-Ni[bn(TFA)$_2$], 37534-27-3; *meso*-Ni[bn(TFA)$_2$], 37534-28-4; *meso*-Pd[bn(TFA)$_2$], 37534-29-5; (±)-Pd[bn(TFA)$_2$], 37534-30-8.

Acknowledgments. We wish to thank Professor R. Belcher and Dr. W. I. Stephen (University of Birmingham, Birmingham, Great Britain) for their interest in this work, Dr. S. Hirozawa and the Wyandotte Chemical Corp. for a gift of 2,3-butylenediamine, and Mr. A. Struck (Perkin-Elmer Corp.) for mass spectra obtained on the RMS.4 mass spectrometer. This work was also supported by the National Science Foundation (Grant GP-31749) and a University of Massachusetts Faculty Research Grant.

---

(28) D. Barnes, W. G. Henderson, E. F. Mooney, and P. C. Uden, *J. Inorg. Nucl. Chem.*, **33**, 2799 (1971).