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Complexes of 1,8-Naphthyridines. XII. Transition Metal Nitrate Complexes of 1,8-Naphthyridine[1a]

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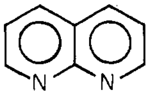
Transition metal nitrate complexes of the type $M(napy)_2(NO_3)_2$ where M = Mn, Co, Ni, Cu, Zn, Cd and napy is 1,8-naphthyridine have been synthesized. Methods used for the characterization of the compounds include elemental analyses, molar conductances, magnetic moments, and electronic, pmr, and infrared spectroscopies. A comparison with the analogous $M(NO_3)_4{}^{2-}$ and $M(napy)_4{}^{2+}$ complexes is made. From these considerations the Mn, Co, Zn, and Cd derivatives appear to be the first examples of neutral, mixed-ligand eight-coordinate complexes of these metals while the Ni and Cu complexes possess a different environment. A polymeric octahedral structure involving bridging nitrate groups is likely for the Cu complex.

Introduction

Eight-coordinate transition metal complexes are a rare occurrence when the electronic configuration of the metal is d^3 or greater.[2] Perhaps the best known examples are the various nitrate complexes in which the metal is surrounded by four bidentate nitrate groups. Bergman and Cotton[3] have studied the eight-coordinate dodecahedral structure of $[As(C_6H_5)_4]_2[Co(NO_3)_4]$; Drummond and Wood[4] have shown that the species $Mn(NO_3)_4{}^{2-}$ and $Zn(NO_3)_4{}^{2-}$ are also eight-coordinate; and King, *et al.*,[5] have shown that Fe(III) can achieve eight-coordination as $Fe(NO_3)_4^-$. Cu(II) and Cd(II) are eight-coordinate in the compounds $Ca[M(O_2CCH_3)_4]\cdot 6H_2O$ where M = Cu or Cd.[6] Recently Hendricker and Bodner[7,8] have reported the syntheses of the series of complexes $M(napy)_4(ClO_4)_2$ where M = Mn, Fe, Co, Ni, Cu, Zn, Pd, Cd, and napy is the bidentate nitrogen heterocycle 1,8-naphthyridine. Crystallographic data have proven that the Fe complex of this series possesses eight-coordinate, distorted dodecahedral geometry.[9] Success in achieving high coordination numbers with napy has not been limited to transition metal ions. Reaction of napy with lanthanide nitrates and perchlorates has yielded the complexes $Ln(napy)_3(NO_3)_3$,[10] where Ln = La-Nd, and $Ln(napy)_6(ClO_4)_3$,[11] where Ln = La-Pr, which apparently exhibit the coordination number 12. Therefore, we have synthesized metal nitrate complexes of napy in an effort to achieve the first examples of mixed-ligand, neutral eight-coordinate species with the transition metals Mn-Zn.



napy

Experimental Section

Materials. Manganese nitrate hexahydrate was purchased from Alfa Inorganics; cobalt nitrate hexahydrate and nickel nitrate hexahydrate were purchased from Fisher Scientific Co.; copper nitrate trihydrate and zinc nitrate hexahydrate were purchased from J. T. Baker Chemical Co.; cadmium nitrate tetrahydrate was purchased from Mallinckrodt Chemical Works; all were used without further purification. Practical grade 2,2-dimethoxypropane (dmp) and spectral grade nitromethane were obtained from Eastman Chemical Co. Commercially available absolute ethanol and ethyl acetate, stored over molecular sieves, were used in the preparation of the complexes. Purity of 1,8-naphthyridine, prepared by the method of Paudler and Kress,[12] was verified by pmr spectroscopy.

Instrumentation. The infrared (4000-200 cm^{-1}) spectra were obtained with a Perkin-Elmer Model 621 double-beam grating spectrophotometer on Nujol-Fluorolube mulls supported between sodium chloride or polyethylene windows. All spectra were calibrated with polystyrene film. An Industrial Instruments Model RC-16B2 conductance bridge was used to determine the conductivity of nitromethane solutions of the complexes. The Sargent Model S-29885 cell was calibrated with a standard KCl solution prepared with conductance water. Magnetic moments were obtained at 25° using the Faraday apparatus described by DuBois and Meek.[13] Diamagnetic corrections for the metal and nitrate ions were obtained from Selwood.[14] A value of -86.8×10^{-6} cgsu was measured for napy. Solution electronic absorption spectra (1600-380 nm) were recorded on spectral grade nitromethane solutions of the complexes in matched 1-, 5-, or 10-cm quartz cells using a Cary Model 14 recording spectrophotometer. Diffuse reflectance spectra (1100-320 nm) were measured on finely ground pure solids with a Beckman DU spectrophotometer equipped with a Beckman Model 2580 reflectance attachment using magnesium carbonate as the reference. A Varian Model HA-100 nmr spectrometer was used to obtain the pmr spectra of nitromethane solutions of selected complexes with tetramethylsilane as the internal standard. Carbon, hydrogen, and nitrogen analyses were ascertained by combustion.

Preparations. $M(C_8H_6N_2)_2(NO_3)_2$ (M = Mn, Co, Ni, Cu, Zn, Cd). A solution of 0.5 mmol of the hydrated metal salt in 15 ml of absolute ethanol was dehydrated by adding 5 ml of dmp and stirring for 3 hr. To this solution was added 2.0 mmol of napy in 10 ml of absolute ethanol, and the resulting mixture was stirred for 2 days. All complexes except Ni precipitated within 15 min. The Ni solution was evaporated under reduced pressure to 10 ml; then 25 ml of ethyl acetate was added and the solution was heated and stirred for several minutes until a precipitate formed. All products were collected by filtration, washed with 60 ml of anhydrous ethyl ether, and dried *in vacuo* at 110° over phosphorus pentoxide for 2-5 days.

Results and Discussion

The analytical data for the complexes listed in Table I indicate that two molecules of ligand are associated with

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(2) S. J. Lippard, *Progr. Inorg. Chem.*, 8, 114 (1967).

(3) J. G. Bergman and F. A. Cotton, *Inorg. Chem.*, 5, 1208 (1966).

(4) J. Drummond and J. S. Wood, *J. Chem. Soc. A*, 226 (1970).

(5) B. T. King, N. Logan, A. Morris, and S. C. Wallwork, *Chem. Commun.*, 554 (1971).

(6) D. A. Langs and C. R. Hare, *Chem. Commun.*, 890 (1967).

(7) D. G. Hendricker and R. L. Bodner, *Inorg. Nucl. Chem. Lett.*, 6, 187 (1970).

(8) (a) R. L. Bodner and D. G. Hendricker, *Inorg. Nucl. Chem. Lett.*, 6, 421 (1970); (b) *Inorg. Chem.*, 12, 33 (1973).

(9) P. Singh, A. Clearfield, and I. Bernal, *J. Coord. Chem.*, 1, 29 (1971).

(10) R. J. Foster and D. G. Hendricker, *Inorg. Chim. Acta*, 6, 371 (1972).

(11) R. J. Foster, R. L. Bodner, and D. G. Hendricker, *J. Inorg. Nucl. Chem.*, in press.

(12) W. W. Paudler and T. J. Kress, *J. Org. Chem.*, 32, 832 (1967).

(13) T. D. DuBois and D. W. Meek, *Inorg. Chem.*, 6, 139 (1967).

(14) P. W. Selwood, "Magnetochemistry," 2nd ed, Interscience, New York, N. Y., 1956, p 78.

Table I. Analytical Data and Physical Properties for $M(napy)_2(NO_3)_2$

	Analysis, %							Conductivity data[a]	
M	Calcd	Found	Calcd	Found	Calcd	Found	Color	Λ(molar), cm^2 mhos	Concn × 10^3, *M*
Mn	43.86	43.74	19.02	19.14	2.79	2.76	White	25	0.57
Co	43.35	43.51	18.96	19.02	2.73	2.68	Rose	34	0.99
Ni	43.37	43.21	18.97	18.99	2.74	2.69	Lt green	59	1.01
Cu	42.90	42.99	18.77	18.75	2.71	2.50	Blue	66	0.47
Zn	42.73	42.63	18.69	18.68	2.70	2.66	White	39	0.56
Cd	38.68	38.77	16.92	16.91	2.44	2.24	White	27	0.68

[a] Values obtained in nitromethane solutions at 25°.

Table II. Selected Infrared Absorptions for 1,8-Naphthyridine and $M(napy)_2(NO_3)_2$ Complexes[a]

	M						
napy	Mn	Co	Ni	Cu	Zn	Cd	Assignment
1556 s	1581 s	1576 s	1574 s	1579 s	1576 s	1582 s	Skel str
1128 s	1136 s	1139 s	1130 s	1134 s	1137 s	1135 s	Skel bend
			1149 m	1141 s			
1045 s	1056 m	1057 m	1061 w	1059 s	1060 s	1056 m	
			1071 m				
1026 s	1031 vs	1029 vs	1041 s	1032 m	1026 vs	1030 vs	Skel str
760 vs	777 vs	779 vs	775 s	773 m	783 vs	777 vs	Skel str
			787 m	786 vs			
600 m	620 s	621 s	625 m	625 s	629 s	618 s	Ligand def
403 s	420 s	421 s	420 s	420 s	420 s	418 s	Ligand def
			429 s				
	264 sh	327 sh	287 s, br	333 vs	286 vs		ν(M-O)
	252 sh	261 sh	256 s	302 w, sh	247 s		
	233 s, br	251 s, br					
	210 sh	222 sh	236 sh	271 s	220 sh		ν(M-N)

[a] Key: s, strong; m, medium; w, weak; v, very; sh, shoulder; br, broad.

each metal. The molar conductivity values (Table I) show that for Mn, Co, Zn, and Cd both nitrate groups are also coordinated to the metal. Conductivity values of 1:1 electrolytes in nitromethane range from 75 to 95 for 10^{-3} *M* solutions,[15] and according to Nathan, *et al.*,[16] values for nonelectrolytic species can reach as high as 50. The molar conductivity data for the Ni and Cu complexes reveal that some dissociation in solution is occurring.

All the compounds are air stable and were stored over $CaSO_4$ to prevent any possible adsorption of water.

The infrared spectra of the complexes from 4000 to 200 cm^{-1} were recorded and analyzed. No bands indicating the presence of water were found. Vibrational modes from 1600 to 650 cm^{-1} have been assigned for free napy,[17] while absorptions from 650 to 400 cm^{-1} are considered ligand deformation modes. The skeletal vibrations which undergo significant shifts in frequency upon coordination are listed in Table II, along with new bands observed below 350 cm^{-1}. The positions of the ligand bands agree well with those observed for $Fe(napy)_4(ClO_4)_2$[8b] in which napy has been shown by crystallographic studies to be bidentate.[9] Splitting of some of the ligand bands in the Ni and Cu complexes is perhaps indicative of a slightly different coordination environment for napy in these compounds relative to the rest of the series.

The new absorption occurring at the lowest frequency was assigned to ν(M-N). The positions are similar to those of the ν(M-N) reported for the $M(napy)_4(ClO_4)_2$ series[8b] and confirmed by Hutchinson.[18] This band follows the Irving-Williams order of stability (Mn < Co < Ni < Cu > Zn[19]) as would be expected for ν(M-N). The other low-frequency absorptions are assigned to ν(M-O) since bands in this region are characteristic of a covalent metal-nitrate bond.[20,21]

The observed nitrate frequencies are listed in Table III. Assignments are based on C_{2v} symmetry for bidentate nitrate.[22,23] Both mono- and bidentate coordination of the nitrate group reduce the symmetry of the free nitrate from D_{3h} to C_{2v}. Thus, the number of infrared-active modes is the same for both cases and cannot serve to distinguish the manner of coordination.

The magnitude of separation of the ν_1 and ν_4 frequencies, Δ, is a measure of the dissymmetry in the nitrate group[24] and has been used as a measure of the covalency in the metal-nitrate bond. The position of ν_1 which is influenced by the polarizing ability of the cation and the coordination environment around the metal has been observed to occur from 1450 to 1600 cm^{-1}.[25-27] The Δ values for the napy complexes (Table III) of Mn, Co, and Zn are similar to those of the eight-coordinate[3,4] $Mn(NO_3)_4^{2-}$ (180)[28] and $Co(NO_3)_4^{2-}$ (177)[28] while the weaker polarizing Cd exhibits a lower Δ value in its napy complex. The Δ value for the $Cu(napy)_2(NO_3)_2$ species is also quite similar to the non-eight-coordinate[3] $Cu(NO_3)_4^{2-}$ (175).[28] The Δ value of 195[28] for the octahedral $Ni(NO_3)_4^{2-}$ suggests much greater covalency than for the $Ni(napy)_2(NO_3)_2$ complex.

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(15) W. J. Geary, *Coord. Chem. Rev.*, 7, 81 (1971).

(16) L. C. Nathan, J. H. Nelson, G. L. Rich, and R. O. Ragsdale, *Inorg. Chem.*, 8, 1494 (1969).

(17) W. L. F. Armarego, G. B. Barlin, and E. Spinner, *Spectrochim. Acta*, 22, 117 (1966).

(18) B. Hutchinson, private communication.

(19) H. Irving and R. J. P. Williams, *J. Chem. Soc.*, 3192 (1952).

(20) R. H. Nuttall and D. W. Taylor, *Chem. Commun.*, 1417 (1968).

(21) J. I. Bullock and F. W. Parrett, *Chem. Commun.*, 157 (1969).

(22) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, N. Y., 1963, p 93.

(23) J. R. Ferraro, "Low Frequency Vibrations of Inorganic and Organic Compounds," Plenum Press, New York, N. Y., 1971, p 79.

(24) J. R. Ferraro, *J. Inorg. Nucl. Chem.*, 10, 319 (1959).

(25) J. H. Forsberg and T. Moeller, *Inorg. Chem.*, 8, 883 (1969).

(26) L. J. Charpentier and T. Moeller, *J. Inorg. Nucl. Chem.*, 32, 3575 (1970).

(27) C. C. Addison and W. B. Sympson, *J. Chem. Soc.*, 598 (1965).

(28) D. K. Straub, R. S. Drago, and J. T. Donoghue, *Inorg. Chem.*, 1, 848 (1962).

Table III. Combination Bands and Vibrational Modes for C_{2v} Nitrate in $M(napy)_2(NO_3)_2$[a]

M	$\nu_2 + \nu_5$	$\nu_2 + \nu_6$	Sepn	ν_1	ν_4	ν_2	ν_3	ν_5	ν_6	$\nu_1 - \nu_4$
Mn	1770 (1773)	1729 (1731)	41 (42)	1459 vs, br	1294 vs	1031 vs	820 s	744 s 740 s	700 w	165
Co	1772 (1776)	1726 (1731)	46 (45)	1470 vs, br	1295 vs	1030 vs	814 s	749 s 742 s	701 w	175
Zn	1763 (1763)	1733 (1732)	30 (31)	1464 vs	1298 vs, br	1025 vs	808 vs	738 s	707 w	166
Cd	1769 (1767)	1732 (1732)	37 (35)	1450 vs, br	1293 vs	1030 vs	818 s	737 s	702 vw	157
Ni	1780 (1776) 1761, 1743	1717 (1724)		1445 sh	1295 vs	1021 vs	816 m	755 s	703 w	150
Cu	1751 (1756) 1799, 1769	1722 (1723)		1470 vs	1290 vs, br	1014 vs	810 vs	747 s 738 m	709 w	180

[a] Key: s, strong; m, medium; w, weak; v, very; sh, shoulder; br, broad. Values in parentheses are calculated from the observed positions of the appropriate bands. Where a doublet was observed for ν_5 an average value was used.

The combination band region of 1700-1800 cm^{-1} has been shown to be helpful in differentiating between the types of nitrate coordination based on the number and/or separation between bands.[29,30] Ionic nitrate exhibits one band; two bands are expected for either bidentate or monodentate coordination; and mixed forms of coordination result in multiple absorptions between 1700 and 1800 cm^{-1}. The different magnitude of combination band separation for monodentate nitrate of 5-26 cm^{-1} and for bidentate nitrate of 20-66 cm^{-1} as confirmed by Raman studies[31] allows one to differentiate between these two possible modes of coordination.[30]

The combination band data for the $M(napy)_2(NO_3)_2$ complexes (Table III) show the Mn, Co, Zn, and Cd compounds possess solely bidentate nitrate groups. The eight-coordinate tetranitrato species of Mn, Co, and Zn also show similar combination band separation, confirming the bidentate nature of the nitrate groups for both series of complexes.[30] Although solid-state effects may produce further splitting of the combination bands, the three or more absorption bands observed for $Cu(NO_3)_4^{2-}$ and $Ni(NO_3)_4^{2-}$ have been interpreted as being indicative of mixed-bonded nitrate.[30] Thus the four bands observed in the 1700-1800-cm^{-1} region for the $M(napy)_2(NO_3)_2$ (M = Cu, Ni) complexes may result from the presence of more than one type of nitrate. Limited solubility of the $Cu(napy)_2(NO_3)_2$ compound in nitromethane relative to the other analogs and a band at 1799 cm^{-1} suggest the possibility of a polymeric bridged structure for the napy complex.

The observed and calculated values for the separation between the two principal combination modes closely correspond (Table III). The slight differences between these values can be attributed to error in the position reported for ν_2, which is expected since ν_2 and a ligand mode both occur at the same or similar energy. Agreement between the observed and calculated combination values is very good in comparison with data of other nitrate compounds.[29]

The magnetic moments of the cobalt, nickel, and copper nitrate complexes of napy are listed in Table IV. The moment for the Co complexes is "tetrahedral-like"[32] as are the moments for $Co(NO_3)_4^{2-}$ (4.50 BM)[33] and $Co(napy)_4^{2+}$ (4.74 BM).[8b] No definitive range of moments for species of dodecahedral geometry exists; however, it is probably an overlap of octahedral and tetrahedral values. The Ni complex has an "octahedral-like" moment,[32,34] similar to the corresponding tetranitrato (3.15 BM)[28] and $(napy)_4$ (3.35 BM)[8b] complexes. The new copper complex has a moment which falls between that of $Cu(NO_3)_4^{2-}$ (1.93 BM)[28] and $Cu(napy)_4^{2+}$ (2.15 BM).[8b]

Table IV. Magnetic and Electronic Spectral Data for $M(napy)_2(NO_3)_2$

					Soln[b]			Solid	
M	$10^6 \chi$, cgsu	$10^3 \chi_m$, cgsu	$10^3 \chi'_m$,[a] cgsu	μ_{eff}, BM	λ, nm	ν, kK	ε, M^{-1} K^{-1}	λ, nm	ν, kK
Co	19.53	8.61	8.88	4.60	1056	9.47	21.4	1050	9.52
					537	18.62	209.2	515	19.42
Ni	9.40	4.17	4.39	3.23	1127	8.87	6.2	*c*	
					785	12.74	0.6	790	12.66
					648	15.43	13.7	660	15.15
Cu	3.16	1.42	1.64	1.98	675	14.81	49.6	630	15.87

[a] χ'_m values corrected for diamagnetic contribution of metal, nitrate, and napy. [b] Data obtained at λ_{max}. [c] Spectra not investigated at >1100 nm.

The electronic spectral data of the new Co, Ni, and Cu complexes for solution (1600-380 nm) and solid (1100-320 nm) samples are summarized in Table IV. Originally the spectrum of $Co(NO_3)_4^{2-}$ was interpreted as indicating a tetrahedral environment for the cobalt atom,[33] but recent studies[35] have revealed that it is only coincidental that the spectrum is similar to that of a tetrahedral species and that it is generally not correct to interpret the electronic spectra of dodecahedral, eight-coordinate complexes using a tetrahedral model. Both the solution and solid spectra of $Co(napy)_2(NO_3)_2$ exhibit two bands. In solution these bands shift to slightly higher wavelengths. The positions of the bands are nearly superimposable with those of the corresponding eight-coordinate tetranitrato[28] and $(napy)_4$[8b] species suggesting a similar ligand field strength for napy and nitrate with Co(II). The ϵ_{max} values lie between these two extremes, but are closer to those of $Co(napy)_4^{2+}$. Slightly distorted Co(II) complexes such as $Co(2,7\text{-}(CH_3)_2napy)_3(ClO_4)_2$[36] exhibit similar band positions which are much less intense for ν_3, ${}^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$, $\epsilon_{max} < 40$.

The band positions in the spectra of $Ni(napy)_2(NO_3)_2$ in solution and solid are quite similar and can readily be interpreted in terms of octahedral Ni(II).[37] The positions and intensities of the absorptions are much like the octahedral $Ni(NO_3)_4^{2-}$ [28] and $Ni(2,7\text{-}(CH_3)_2napy)_3(ClO_4)_2$[36] including the appearance of the forbidden ${}^1E_g(D) \leftarrow {}^3A_{2g}(F)$ transition. The positions of the absorptions and the mag-

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(29) N. F. Curtis and Y. M. Curtis, *Inorg. Chem.*, 4, 804 (1965).

(30) A. B. P. Lever, E. Mantovani, and B. S. Ramaswamy, *Can. J. Chem.*, 49, 1957 (1971).

(31) J. R. Ferraro, C. Cristallini, and I. Fox, *J. Inorg. Nucl. Chem.*, 29, 139 (1967).

(32) B. N. Figgis and J. Lewis in "Technique of Inorganic Chemistry," Vol. 4, H. B. Jonassen and A. Weissberger, Ed., Interscience, New York, N. Y., 1965, p 166.

(33) F. A. Cotton and T. G. Dunne, *J. Amer. Chem. Soc.*, 84, 2013 (1962).

(34) A. P. B. Lever, *Inorg. Chem.*, 4, 763 (1965).

(35) C. D. Garner and F. E. Mabbs, *J. Chem. Soc. A*, 1711 (1970).

(36) D. G. Hendricker and R. L. Bodner, *Inorg. Chem.*, 9, 273 (1970).

(37) A. B. P. Lever, "Inorganic Electronic Spectroscopy," Elsevier, New York, N. Y., 1968, Chapter 9.

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

The single band observed in the solid spectrum of $Cu(napy)_2(NO_3)_2$ 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 $Fe(napy)_4^{2+}$.[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 $Cu(NO_3)_4^{2-}$ [28] and $Cu(napy)_4^{2+}$.[8b]

The pmr spectrum of $Zn(napy)_2(NO_3)_2$ 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: $Zn(napy)_2(NO_3)_2$, 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; $Mn(napy)_2(NO_3)_2$, 37475-80-2; $Co(napy)_2(NO_3)_2$, 37454-25-4; $Ni(napy)_2(NO_3)_2$, 37189-82-5; $Cu(napy)_2(NO_3)_2$, 37189-81-4; $Zn(napy)_2(NO_3)_2$, 37454-26-5; $Cd(napy)_2(NO_3)_2$, 37454-24-3.

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[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.

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

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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 $M^{III}(\beta\text{-dik})_3$ [1-6] (dik = diketonate) and to a limited extent $M^{II}(\beta\text{-dik})_2$,[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

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[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).