3358 *Inorg. Chem.* **1991**, *30*, 3358-3361

Notes

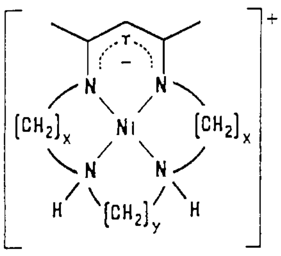
Contribution from the Department of Chemistry,
Wright State University, Dayton, Ohio 45435

Nickel(II) and Cobalt(II) Complexes with 2,4-Pentanedionate and Tetraamine Ligands: Synthesis and Structural Characterization

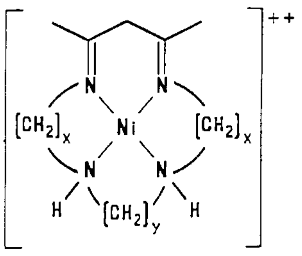
Jeffrey L. Moler[†] and Sue C. Cummings*

Received August 21, 1990

Over the past twenty-five years, much effort has been directed toward the synthesis of macrocyclic metal complexes.[1-5] The ability of certain metal ions to direct the course of such reactions and facilitate ring closure has been termed the "coordination template effect".[5,6] In 1970, we[7,8] reported the template synthesis of a macrocyclic Ni(II) complex containing a uninegative ligand formed via condensation of triethylenetetramine with 2,4-pentanedione (structure I, where $x = y = 2$). Subsequent studies[9] showed that the γ-carbon could be protonated under acidic conditions to yield a complex with the corresponding neutral macrocyclic ligand (structure II) that contains localized diimine linkages. Over the next several years, work in our laboratory centered on studying the scope of this macrocyclization process by using different metal ions such as Cu(II)[10,11] and Co(II)[12] as template ions, along with tetradentate phosphineamines[13,14] and tetraamines of different chain lengths. The mechanism of ring closure also was of interest to us, especially since the yields never exceeded 70%, and highest yields of macrocyclic products usually were obtained when twice the stoichiometric amounts of β-diketones were added. This latter observation is consistent with the possible formation of diazepine intermediates, as reported by Hideg and Lloyd.[15]



I

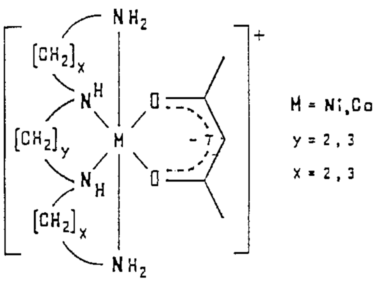


II

In order to try to understand the course of macrocycle formation, we isolated and characterized the side products that formed. As a result of earlier studies in our laboratory, two complexes of stoichiometry $[Ni(2,3,2\text{-}N_4)(acac)]I$ and $[Ni(3,2,3\text{-}N_4)(acac)]I$, structure III, were discovered.[16] We now wish to report the results of a broader study[17] designed (1) to investigate the conditions necessary to optimize the synthesis of the noncondensed tetraamine–diketonate complexes and (2) to see if these noncyclic products could be used as precursors to the macrocyclic complexes. While this work was in progress, synthesis of $[Ni(2,2,2\text{-}N_4)(acac)]ClO_4$ and $[Ni(2,3,2\text{-}N_4)(acac)]ClO_4$ were independently reported.[18]

Experimental Section

Materials. All metal salts, organic reagents, and solvents were reagent grade. Solvents were purified by using established procedures.[19]



III

Measurements. Infrared spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer by employing Nujol mull techniques. Molar conductivities were calculated from electrical resistance measurements of 10^{-3} M methanol solutions using a Beckman Model RC-19 Conductivity Bridge. Near-infrared, visible, and ultraviolet spectra were recorded on 10^{-1}–10^{-4} M solutions and in the solid state by the diffuse-reflectance technique[20] with a Cary Model 14 recording spectrophotometer with absolute methanol and tetrachloroethylene as solvents. Room temperature magnetic susceptibility data were obtained by the Faraday technique with a Cahn RG recording electrobalance and an Alpha electromagnet with 4-in. constant-force pole caps. Measurements were taken at approximately 8 and 10 kG. The powder diffraction patterns were obtained by using a Seifert-Scintag automated powder diffractometer (PADII) equipped with a Guinier camera to record the powder patterns.[21] The samples were contained in capillaries during analyses. All carbon, hydrogen, and nitrogen analyses were performed by Midwest Microlabs, Ltd., Indianapolis, IN, except for $[Ni(3,2,3\text{-}N_4)(acac)]PF_6$, which was analyzed at Wright State University, Dayton, OH.

Syntheses. General Comments. Nickel(II) reactions were performed under normal atmospheric conditions. Cobalt(II) reactions were carried out under nitrogen by using Schlenk glassware. The purple Ni(II) complexes were dried in vacuo at 100 °C for 12 h, while the orange Co(II) compounds were dried for 20 h at room temperature before they were analyzed. Yields varied from 35 to 75%. All complexes gave satisfactory elemental analyses for the noncondensed formulations proposed.

(1) Typical Preparation of a Nickel(II) Complex. (*N,N'*-Bis(2-aminoethyl)-1,3-propanediamine)(2,4-pentanedionato)nickel(II) Hexafluorophosphate ($[Ni(2,3,3\text{-}N_4)(acac)]PF_6$). A 4.98-g sample (0.02 mol) of nickel acetate tetrahydrate was dissolved in 100 mL of distilled,

---

* To whom correspondence should be addressed.

[†] Currently assigned to AFIT/CIRD, Air University, Air Force Institute of Technology, Wright-Patterson AFB, OH 45433-6583 (Department of Chemistry, University of Iowa, Iowa City, IA).

(1) Busch, D. H. *Helv. Chim. Acta, Fasc. Extraordinarius, Alfred Werner* **1967**, *50*, 174.
(2) Lindoy, L. F.; Busch, D. H. *Prep. Inorg. React.* **1971**, *6*, 1.
(3) Melson, G. A. *Coordination Chemistry of Macrocyclic Compounds*; Plenum Press: New York, 1979; references therein.
(4) Busch, D. H. *Acc. Chem. Res.* **1978**, *11*, 392.
(5) Thompson, M. C.; Busch, D. H. *J. Am. Chem. Soc.* **1964**, *86*, 3651.
(6) Busch, D. H. *Adv. Chem. Ser.* **1963**, *No. 37*, 16.
(7) Cummings, S. C.; Sievers, R. E. *J. Am. Chem. Soc.* **1970**, *92*, 215.
(8) Cummings, S. C.; Sievers, R. E. *Inorg. Chem.* **1970**, *9*, 1131.
(9) Elfring, W. H.; Rose, N. J. *Inorg. Chem.* **1975**, *14*, 2759.
(10) Martin, J. G.; Wei, R. M. C.; Cummings, S. C. *Inorg. Chem.* **1972**, *11*, 475.
(11) Martin, J. G.; Cummings, S. C. *Inorg. Chem.* **1973**, *12*, 1477.
(12) Roberts, G. W.; Cummings, S. C.; Cunningham, J. A. *Inorg. Chem.* **1976**, *15*, 2503.
(13) Scanlon, L. G.; Tsao, Y. Y.; Cummings, S. C.; Toman, K.; Meek, D. W. *J. Am. Chem. Soc.* **1980**, *102*, 6849.
(14) Scanlon, L. G.; Tsao, Y. Y.; Toman, K.; Cummings, S. C.; Meek, D. W. *Inorg. Chem.* **1982**, *21*, 1215.
(15) Hideg, K.; Lloyd, D. *Chem. Commun.* **1970**, 929.
(16) Martin, J. G. M.S. Thesis, Wright State University, Aug 1971.
(17) Taken in part from the M.S. Thesis of J. L. Moler, Wright State University, March 1982.
(18) Curtis, N. F.; Milestone, N. B. *Aust. J. Chem.* **1974**, *27*, 1167.
(19) Perrins, D. D.; Armarego, W. L. F.; Perrins, D. R. *Purification of Laboratory Chemicals*; Pergamon Press: London, 1980.
(20) Lee, R. H.; Griswold, E.; Kleinberg, J. *Inorg. Chem.* **1964**, *3*, 1279.
(21) Access to this equipment in the Department of Chemistry of Texas A&M University, College Station, TX, is gratefully acknowledged.

0020-1669/91/1330-3358$02.50/0 © 1991 American Chemical Society

deionized water. To this light green solution was added 3.21 g (0.02 mol) of *N,N'*-bis(2-aminoethyl)-1,3-propanediamine. The solution turned blue-green and then red-brown. The solution was stirred for 15 min before a slight excess, 2.50 g (0.025 mol), of 2,4-pentanedione was added. The color of the solution changed to purple after 10 min of stirring. The pH was adjusted to 11.5 by the addition of 3 mL of 5 M sodium hydroxide solution. Stirring was continued for 16 h. An aqueous solution of 4.08 g (0.025 mol) of ammonium hexafluorophosphate was added rapidly to the stirred solution, resulting in the formation of a purple precipitate. The precipitate was isolated by filtration and then washed and dried with ethanol and diethyl ether. The precipitate was recrystallized from hot methanol to give violet crystals. Yield: ~62%. Reaction protocols were similar for the other Ni(II) complexes except that, in the case of the iodide derivatives, KI was added as the source of the counterion.

(2) Typical Preparation of a Cobalt(II) Complex. (*N,N'*-Bis(2-aminoethyl)-1,3-propanediamine)(2,4-pentanedionato)cobalt(II) Hexafluorophosphate ([Co(2,3,2-N$_4$)(acac)]PF$_6$). A 4.98-g sample (0.02 mol) of cobalt acetate tetrahydrate was dissolved in 50 mL of water in a 200-mL Schlenk flask, and the solution was heated to boiling with nitrogen bubbling through the solution. After 30 min, a Schlenk dropping funnel was connected to the flask and 3.21 g (0.02 mol) of *N,N'*-bis(2-aminoethyl)-1,3-propanediamine in 30 mL of water was deaerated for 30 min above the reaction vessel. The tetraamine was then added with stirring, and the solution turned a dark orange-red. Then 2.00 g (0.02 mol) of 2,4-pentanedione in 30 mL of water was deaerated for 30 min in the addition funnel. This solution was then added with stirring to the reaction mixture. The resulting clear solution was bright orange. Then, 3 mL of 5 M sodium hydroxide solution in 30 mL of water was deaerated for 30 min and then added to the reaction mixture to adjust the pH to 11–12. The solution was bluish purple. The solution was stirred for 30 min while 4.08 g (0.02 mol) of ammonium hexafluorophosphate in 30 mL of water was deaerated in the funnel. The hexafluorophosphate salt was added through the dropping funnel, and the solution was stirred for 16 h. During this time, orange crystals developed. The orange crystals were filtered out on the Schlenk line and dried in vacuo at room temperature for 6 h. The precipitate was recrystallized from methanol, and the bright orange crystals obtained were filtered out under nitrogen. The compound, while under vacuum in the Schlenk filter, was transferred to a glovebox for weighing and storage. Yield: ~35%. The remaining cobalt(II) complexes were prepared in a similar manner except for [Co(3,2,3-N$_4$)(acac)]PF$_6$, where the 2,4-pentanedione was added in the form of its sodium salt. Iodide complexes were precipitated by addition of KI.

Results and Discussion

(1) Characterization of Nickel(II) Complexes. Infrared spectra of the complexes provide the primary source of structural evidence for the noncondensed nature of the 2,4-pentanedionato tetraamine complexes. Since the complexes were dried in vacuo at 100 °C and the mulls prepared under anhydrous conditions, no bands due to water are present; however, several strong bands characteristic of the new complexes are observed at 3400–3100, ~1590, and ~1515 cm^{-1}. The three highest energy absorptions in the 3300-cm^{-1} region are assigned to the symmetric and asymmetric NH$_2$ and symmetric NH stretching vibrations.[22,23] The amine bands in the iodide complexes are at lower energies than those observed for the hexafluorophosphate derivatives due to hydrogen bonding with the iodide anion. A strong, broad band at ~1590 cm^{-1} is due to the C$\cdots$O stretching mode of the β-diketone moiety, which has been shifted to this lower energy by coordination to the metal ion.[23] The strong absorption at ~1515 cm^{-1} is assigned to the bending mode of the primary amine. The presence of bands attributable to both the NH$_2$ and β-diketone moieties in these compounds and the absence of bands at ~1660 and ~1550 cm^{-1}, which are characteristic of imine, C=N, or iminato, C$\cdots$N, linkages as reported in spectra of the [M(dieneN$_4$)]$^{2+}$ or [M(dienatoN$_4$)]$^+$ macrocyclic complexes,[7,8,10-14] indicates that neither Schiff base condensation nor cyclization has occurred. Strong bands at 850 and ~560 cm^{-1} indicate the presence of PF$_6^-$ and are assigned to the stretching and bending modes of the noncoordinated anion.[24] No bands associated with the iodide anion are expected nor are they observed. The presence of triiodide is ruled out by the elemental analyses. Steric effects imposed by the length of the tetraamine and the size of the anion provide different conformational environments, and thus the various–CH overtones give rise to unique patterns in the fingerprint region (1300–900 cm^{-1}) for each complex.

Room-temperature magnetic moments of the nickel(II) complexes are of the order of ~3.2 μ_B. These values are typical of high-spin, octahedral Ni(II), which has two unpaired electrons. Deviation from the spin-only value of 2.83 μ_B indicates some spin–orbit coupling contribution.[25] Molar conductances of the new complexes were measured in dry methanol and ranged from 80 to 115 Ω^{-1} cm^2 mol^{-1}. Such values are typical of 1:1 electrolytes in methanol.[26]

The visible and ultraviolet spectra of these complexes also have been measured in methanol and in the solid state and are reported in Table I. The two bands observed in the visible region: ν_1 at 10700–11040 cm^{-1} ($\epsilon \sim 10$) and ν_2 at 17540–18700 cm^{-1} ($\epsilon \sim 10$) have been assigned to the d–d transitions $^3T_{2g} \leftarrow {}^3A_{2g}$ and $^3T_{1g}(F) \leftarrow {}^3A_{2g}$, respectively. The band at approximately 10800 cm^{-1} exhibits a shoulder on the high-energy side of the absorption at 12660–12790 cm^{-1}, which is attributed to the $^1E_g \leftarrow {}^3A_{2g}$ spin-forbidden transition. While ν_3 ($^3T_{1g}(P) \leftarrow {}^3A_{2g}$) for high-spin, octahedral Ni(II) should appear at ~30000 cm^{-1}, it is obscured by very intense bands in the range 32840–33060 cm^{-1} ($\epsilon \sim$ 10,000), which we have identified as charge-transfer bands. It should be noted that ν_3 may be observed in the solid-state spectrum of one of the new complexes; i.e., [Ni(3,2,3-N$_4$)(acac)]I, where an unassigned transition occurs at 27400 cm^{-1}.

Several parameters that can be calculated from the visible spectra are worth mentioning. First, Dq, which here represents an average ligand field strength, is obtained as $\nu_1/10$. Dq_{av} increases as the carbon chain length of the tetraamine decreases. The strongest field strength, associated with the (2,3,2) backbone, may reflect strain-free coordination of the ligand, which allows more overlap of the nickel orbitals with those of the donor nitrogens. B'_{av} is calculated as 1025 cm^{-1}, which is 95% of the free-ion value (1080 cm^{-1}).[27] This indicates that the nickel electrons are delocalized only to a small extent over the molecular orbitals of the complex.

(2) Characterization of Cobalt(II) Complexes. Visual comparison of the infrared spectra of corresponding cobalt(II) and nickel(II) complexes reveal virtually identical patterns. Examination of the amine stretching vibrations in the 3300-cm^{-1} region shows no broadening that would indicate the presence of lattice water in the cobalt(II) complexes. The characteristic three bands at 3400–3100 cm^{-1} and those at ~1590 and ~1515 cm^{-1}, discussed in the nickel(II) complexes, are present in all of the cobalt(II) spectra. The presence of bands attributable to the coordinated NH$_2$ and β-diketone ligands and absence of bands indicative of imine and iminato moieties indicates that Schiff base condensation has not occurred. Hexafluorophosphate bands again are seen at 850 and ~560 cm^{-1}.[24]

Values of the calculated magnetic moments of the crystalline cobalt(II) complexes are of the order of 4.90–5.08 μ_B. Because octahedral high-spin cobalt(II) complexes have a $^4T_{1g}$ ground state, which is orbitally degenerate, a full orbital contribution to the spin-only value of 3.87 μ_B is expected and results in magnetic moments of 4.80–5.25 μ_B.[28] Molar conductances of the new cobalt complexes were measured in methanol solutions prepared and examined under nitrogen. Values of Λ_M ranged between 90 and 113 Ω^{-1} cm^2 mol^{-1}, confirming that the complexes are 1:1 electrolytes.[26]

---

(22) Conley, R. T. *Infrared Spectroscopy*, 2nd ed.; Allyn and Bacon: Boston, MA, 1972; pp 143–146, 155.

(23) Nakamoto, K. *Infrared Spectra of Inorganic and Coordination Compounds*, 2nd ed.; Wiley: New York, 1970; pp 249–254, 151–156.

(24) Begum, G. M.; Rutenberg, A. C. *Inorg. Chem.* **1967**, *6*, 2212.

(25) Earnshaw, A. *Introduction to Magnetochemistry*; Academic Press: New York, 1968; pp 58–60.

(26) Angelici, R. J. *Synthesis and Technique in Inorganic Chemistry*; Saunders: Philadelphia, PA, 1977; p 213.

(27) Figgis, B. N. *Introduction to Ligand Fields*; Interscience: New York, 1986; p 52.

(28) Reference 25, pp 34 and 35. Figgis, B. N. *Introduction to Ligand Fields*; Interscience: New York, 1966; pp 285–289.

Table I. Observed and Calculated Electronic Spectral Data for $[Ni(N_4)(acac)]X$ Complexes

	abs bands								
	solution[a]			solid state[b]					
compd	λ, nm	ε[c]	ν, cm^{-1}	λ, nm	ν, cm^{-1}	*B′*, cm^{-1}	*Dq*, cm^{-1}	calcd ν, cm^{-1}	assgnts
$[Ni(3,3,3\text{-}N_4)(acac)]PF_6$	935	7.9	10 700	923	10 830			10 700	$^3T_{2g} \leftarrow {}^3A_{2g}$
	789[d]	3.0	12 670[d]	785[d]	12 740[d]				$^1E_g \leftarrow {}^3A_{2g}$
	570	11.4	17 540	556	17 990	1023	1070	17 540	$^3T_{1g}(F) \leftarrow {}^3A_{2g}$
								29 910	$^3T_{1g}(P) \leftarrow {}^3A_{2g}$
	303	10600	33 000	313	31 950				
	260	2110	38 460	262	38 170				
$[Ni(3,2,3\text{-}N_4)(acac)]PF_6$	908	11.3	11 010	904	11 060			11 010	as above
	784[d]	5.8	12 760[d]	785[d]	12 740[d]				
	557	10.2	17 950	551	18 170	1008	1101	17 950	
								30 201	
	305	9990	32 840	309	32 420				
	260	2540	38 460	262	38 240				
$[Ni(2,3,2\text{-}N_4)(acac)]PF_6$	908	13.2	11 010	909	11 010			11 010	as above
	787[d]	6.8	12 710[d]	790[d]	12 660[d]				
	554	9.4	18 070	553	18 100	1064	1101	18 070	
								30 913	
	305	10400	32 840	313	31 950				
	259	2760	38 610	262	38 168				
$[Ni(3,3,3\text{-}N_4)(acac)]I$	933	7.5	10 720	931	10 740			10 720	as above
	786[d]	3.0	12 720[d]	788[d]	12 690[d]				
	570	11.4	17 540	570	17 540	1010	1072	17 540	
								29 767	
	303	10600	33 060	311	32 210				
	260	2120	38 460						
$[Ni(3,2,3\text{-}N_4)(acac)]I$	908	11.8	11 010	893	11 200			11 010	as above
	785[d]	6.3	12 740[d]	790[d]	12 660[d]				
	556	10.2	17 990	547	18 280	1026	1101	17 990	
				365	27 400			30 428	
	303	10000	33 000	308	32 470				
	259	2550	38 610	264	37 880				
$[Ni(2,3,2\text{-}N_4)(acac)]I$	906	11.1	11 040	904	11 060			11 040	as above
	785[d]	7.0	12 740[d]	782	12 790[d]				
	555	9.5	18 020	550	18 180	1020	1104	18 020	
								30 402	
	305	9990	32 840	306	32 730				
	258	2480	38 760	258	38 760				

[a] Solution spectra were obtained by using concentrations of $\sim 5 \times 10^{-3}$ M (methanol) for the low-energy bands and $\sim 1 \times 10^{-3}$ M (methanol) for the high-energy bands. [b] Solid-state spectra were obtained by using the Nujol mull diffuse-transmittance technique. [c] Molar absorptivities, L mol^{-1} cm^{-1}. [d] Spin-forbidden band, shoulder appearing on a major band.

The visible and ultraviolet spectra of methanol and tetrachloroethylene solutions of the cobalt(II) complexes are reported in Table II. The highest energy band for the cobalt(II) species is in the range 34 130–34 600 cm^{-1} ($\epsilon \sim 10000$), which compares well with the charge-transfer band observed at 33 000 cm^{-1} in spectra of the nickel(II) complexes. The only d–d absorption bands that are observed in spectra of the Co(II) complexes occur as follows: ν_1 at 9100–10 420 cm^{-1} ($\epsilon \sim 8$) and ν_2 at 20 370–21 010 cm^{-1} ($\epsilon \sim 40$). Three spin-allowed d–d transitions are expected for octahedral Co(II) unless the field strength of the ligands is such that the $^4A_{2g}$ and $^4T_{1g}(P)$ terms have the same energy. This occurs when the two states cross. Typical values of ν_1, ν_2, and ν_3 for octahedral cobalt(II) are 8000, 20 000, and 22 000 cm^{-1}, respectively.[29] The assignment of ν_1 to the $^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)$ transition is unequivocal; however, depending upon the *Dq*/*B* ratio, ν_2 may be either $^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$ or $^4A_{2g} \leftarrow {}^4T_{1g}(F)$. If ν_2 is assigned to $^4A_{2g} \leftarrow {}^4T_{1g}(F)$, then $Dq = \nu_2 - \nu_1/10$; however, the *Dq* results obtained in this manner do not compare well with the nickel(II) values determined earlier. If the alternative assignment is made as

ν_1: $^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)$ 10 060 cm^{-1}

ν_2: $^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$ 20 620 cm^{-1}

where the energies are the averages of all those observed experimentally for the series of Co(II) complexes, then spectral parameters can be calculated by using a Tanabe–Sugano[30] diagram. For a *Dq*/*B* ratio of 1.4, Dq_{av} = 1108 cm^{-1} and the energies of the $^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$ and $^4A_{2g} \leftarrow {}^4T_{1g}(F)$ transitions are 20 592 and 21 281 cm^{-1}, respectively. The good agreement between the calculated and observed band energies serves to indicate the correctness of the band assignments and confirms that ν_2 is the transition between the $4T_{1g}$ states. In the new cobalt(II) complexes, B'_{av} is calculated as 792 cm^{-1}, which is approximately 70% of the free-ion value (1120 cm^{-1}).[27] This indicates ~30% covalent character in the metal–ligand bonds, which is a significant increase in electron delocalization as compared to the nickel case. In general, *Dq* increases with decreasing carbon chain length in the tetraamine except for the inversion of the $[Co(3,2,3\text{-}N_4)(acac)]PF_6$ and $[Co(2,3,2\text{-}N_4)(acac)]PF_6$ complexes. The total field strength of the N_4O_2 ligand donor set in these complexes is such that the ratio of the bands lies in the proximity of the crossover in energies of the $^4A_{2g}(F)$ and $^4T_{1g}(P)$ terms on the Tanabe–Sugano diagram. The transition to the $^4A_{2g}$ state involves the excitation of two electrons and is expected to be weaker than the other two transitions; hence, masking of the $^4A_{2g}(F) \leftarrow {}^4T_{1g}(F)$ band is not totally unexpected. This phenomenon also has been reported for the bis(pyridine) adduct of (*N*,*N′*-bis(3-isopropylsalicylidene)-1,5-diaminopentane)cobalt(II).[31] The complex exhibited two bands at 10 000 and 17 860 cm^{-1} and was characterized as a high-spin, pseudooctahedral cobalt(II) complex.

The final physical technique used to characterize both the new nickel(II) and cobalt(II) complexes was X-ray powder diffraction.

---

(29) Figgis, B. N. *Introduction to Ligand Fields*; Interscience: New York, 1986; pp 161, 223–225.

(30) Drago, R. S. *Physical Methods in Chemistry*; Saunders: Philadelphia, PA, 1977; pp 383–387.

(31) Hariharan, M.; Urbach, F. L. *Inorg. Chem.* **1971**, *10*, 2667.

Table II. Observed and Calculated Electronic Spectral Data for [Co(N_4)(acac)]X Complexes

	abs bands								
	solution[a]			solid state[b]					
compd	λ, nm	ϵ[c]	ν, cm^{-1}	λ, nm	ν, cm^{-1}	B', cm^{-1}	Dq, cm^{-1}	calcd ν, cm^{-1}	assgnts
[Co(3,3,3-N_4)(acac)]PF_6	1009	8	9910	985	10150			10039	$^4T_{2g} \leftarrow {}^4T_{1g}(F)$
	491	34	20370	476	21010	780	1092	20280	$^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$
								20959	$^4A_{2g} \leftarrow {}^4T_{1g}(F)$
	292	10800	34250						
[Co(3,2,3-N_4)(acac)]PF_6	960	9	10420	979	10220			10543	as above
	476	51	21010	458	21830	820	1149	21320	
								22033	
	292	11000	34250						
[Co(2,3,2-N_4)(acac)]PF_6	995	9	10100	982	10180			10232	as above
	485	50	20620	458	21830	795	1113	20670	
								21362	
	289	7000	34600						
[Co(3,3,3-N_4)(acac)]I	1020	8	9800	1026	9750			10374	as above
	491	31	20370	488	20490	772	1080	20072	
								21174	
	293	9100	34130						
[Co(3,2,3-N_4)(acac)]I	999	8	10010	983	10170			10144	as above
	486	37	20580	468	21370	788	1103	20488	
								21174	
	292	10300	34250						
[Co(2,3,2-N_4)(acac)]I	990	6	10100	990	10100			10232	as above
	482	40	20750	485	20620	795	1113	20670	
								21362	
	292	11200	34250						

[a] Solution spectra were obtained by using concentrations of ~1 × 10^{-1} M (tetrachloroethylene, C_2Cl_4), ~1.0 × 10^{-2} M (methanol), and ~1.0 × 10^{-3} M (methanol), one for each band going from low energy to high energy. [b] Solid-state spectra were obtained by using the Nujol mull diffuse-transmittance technique.[23] [c] Molar absorptivities, L mol^{-1} cm^{-1}.

Both visual and numerical comparison of the diffraction lines show that the patterns are identical and that the compounds are isomorphic.

Conclusions

While there is no doubt that the 12 complexes prepared in this study have pseudooctahedral structures, visible spectra cannot be used to determine whether the compounds exist in the α-cis or β-cis isomeric forms or a mixture thereof. Proton magnetic resonance studies are precluded by the paramagnetic nature of both metal ions. This leaves infrared spectral data as the only source for conjecture.

In the infrared spectra of [M(2,3,2-N_4)(acac)]PF_6 and [M(3,2,3-N_4)(acac)]PF_6, the presence of only one isomer is suggested by the uncomplicated nature of the nitrogen–hydrogen stretching vibrations observed. A mixture of isomers may be indicated by the more complicated patterns of the corresponding iodide salts; however, in these compounds, selective hydrogen bonding of one set of amine protons to the iodide ion causes a shift of some of these stretching vibrations to lower energies. Infrared spectra of the [M(3,3,3-N_4)(acac)]PF_6 and [M(3,3,3-N_4)(acac)]I complexes show the most complicated stretching patterns for the amine protons and are most likely to exist as a mixture of isomers because of greater flexibility associated with longer carbon chains. Indeed, isomer studies of tetraamine complexes[32] have shown that as the chain length increases, the trans form is favored and only the β-cis form exists in the presence of a bidentate ligand. It is likely that the β-cis form dominates in the (3,2,3) and (3,3,3) complexes prepared in this study, but the differences in numbers of IR bands may be due to solid-state effects only.

Attempts to prepare macrocyclic tetraaza complexes via the acid-catalyzed (pH ~ 3) rearrangement of the [Ni(N_4)(acac)]X complexes in aqueous solution were unsuccessful. Three hours of refluxing followed by addition of 1 equiv of KX always resulted in the formation of the corresponding tetraamine, [Ni(N_4)X_2], which was identified on the basis of its infrared spectrum. Under the same conditions, nickel complexes containing similar sexadentate Schiff base ligands do react to form the desired macrocycles.[7,8] This suggests that 2 equiv of β-diketone are necessary for ring closure to occur. This hypothesis was tested by refluxing acidic solutions of the [Ni(N_4)(acac)]X complexes in the presence of an additional 1 equiv of 2,4-pentanedione. Small amounts of the macrocyclic species are produced;[33] however, the mechanism involved here cannot be distinguished from the in situ procedure previously reported.[7,8] The latter procedure continues to provide the best means of synthesis of macrocyclic complexes with uninegative Schiff base ligands.

Acknowledgment. S.C.C. gratefully acknowledges financial support of this investigation by the National Institutes of Health, Grant HL 15640 from the Heart, Lung, and Blood Institute.

Supplementary Material Available: Tables of analytical data along with yields and colors of individual complexes and magnetic susceptibility data (1 page). Ordering information is given on any current masthead page.

---

(32) Alexander, M. D.; Hamilton, G. *Inorg. Chem.* **1969**, *10*, 2131.

(33) Sweitzer, R. K.; Cummings, S. C. *Proceedings of the Undergraduate Science Symposium*; Vol. I, Central State University: Wilberforce, OH 45384, 1984; Vol. I, p 26.

Contribution from the Department of Chemistry,
The University of Texas at Austin, Austin, Texas 78712

A Theoretical Study of the HP_4 Ion

Michael J. S. Dewar* and Ya-Jun Zheng

Received March 8, 1990

Baudler et al.[1] recently reported the reduction of tetraphosphorus (**1**) to an anion (**2** or **3**) which can be regarded as the monoconjugate base from tetraphosphabicyclobutane (**4**). The NMR spectrum of the ion in solution showed three different

---

* To whom correspondence should be addressed at the Department of Chemistry, University of Florida, Gainesville, FL 32611.

0020-1669/91/1330-3361$02.50/0 © 1991 American Chemical Society