clusive. Thus it is possible that the nickel dimethylglyoxime species in an oxidative and basic medium exists as the divalent anion. This would confirm the conclusion reached by Šimek from magnetochemical studies.[16,17]

While the reaction of nickel and dipyridylglyoxime in basic solution produced no species of interest, a highly colored complex is formed in the presence of oxidizing agents. Wave lengths of maximum absorption at 405 and 455 mμ were found. The molar absorptivities at these wave lengths were 15,500 and 14,000, respectively. Molar ratio studies carried out on the system, as shown in Table V, indicated a reacting ratio of 3:1, while ion migration indicated an anionic species. Insofar as the system was investigated, it seems analogous to the Ni(II)–dimethylglyoxime reaction in the presence of oxidizing agents.

TABLE V

MOLE RATIO STUDY OF NICKEL–PYRIDYLGLYOXIME SYSTEM

1×10^{-4} M Ni^{++}; 5×10^{-2} M $K_2S_2O_8$; pH 9.2 buffer

Dioxime ($M \times 10^4$)	Absorbance 405 mμ	495 mμ
1.00	0.49	0.39
2.00	1.08	0.94
3.00	1.45	1.35
4.00	1.51	1.38
5.00	1.51	1.35

[16] M. Šimek, *Coll. Czech. Chem. Commun.*, **26**, 337 (1962).

[17] M. Šimek, *ibid.*, **26**, 461 (1962).

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The Preparation and Properties of Bis-(4-amino-3-pentene-2-ono)-nickel(II)

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Syntheses of bis-(4-amino-3-pentene-2-ono)-nickel(II) in both aqueous and non-aqueous media are described, as are some physical and chemical properties of this new red, diamagnetic nickel(II) chelate. Ultraviolet, visible, and infrared spectral data, solubilities, and reaction with water are discussed. A *trans*-configuration is apparent from the ligand field absorption bands of the spin-paired complex.

Introduction

Considerable interest has been generated in the stereochemistry of nickel(II) complexes with a stoichiometry of four coördinating groups per nickel ion inasmuch as three different structures are observed—planar, octahedral, and tetrahedral. Many of the paramagnetic nickel(II) complexes of this type, once thought to be tetrahedrally coördinated,[1] have been found to be octahedrally coördinated by polymerization. Structural studies include the trimeric anhydrous acetylacetonate,[2] nickel(II) chloride dihydrate,[3] $Ni(NCS)_2(thiourea)_2$,[4] and $Ni(NCS)_2(pyridine)_2$.[5] The same probably is true for the anhydrous nickel(II) salicylaldehyde complex.[6] Tetrahedral paramagnetic complexes of nickel(II) have been prepared through the use of large anions (Cl^-, Br^-, I^-, NO_3^-),[7] which prohibit the more favorable planar and octahedral configurations because of electrostatic repulsions. On the other hand, planar structures have been found for all the red, diamagnetic nickel complexes that have been studied by X-rays,[8] although large chelate rings can be used to distort the planarity.[9]

The β-diketone complexes of nickel have undergone considerable study and for 2,4-pentanedione an aqua, paramagnetic, octahedrally coördinated dihydrate,[10] as well as the green, paramagnetic, octahedral, anhydrous trimer[2] are known. Bulky 1,5-disubstitution on the β-diketone allows the isolation of red, diamagnetic complexes[11] which undoubtedly are planar, and in the case of bis-(2,6-dimethyl-3,5-heptanediono)-nickel-(II) an equilibrium between the red, diamagnetic form and the green, paramagnetic form has been observed.[11]

It has been suggested by Holm[8] that the Ni–O_2N_2 type complexes represent an intermediate situation in bond strength in which the ligand field strength may or may not be sufficient to pair the electron spins. There is considerable data to support this view. It therefore seemed desirable to investigate the Ni–O_2N_2 complex most closely related to the nickel 2,4-pentanedione complexes and one which should have

[1] L. Pauling, "The Nature of the Chemical Bond," 2nd Ed., Cornell Univ. Press, Ithaca, N. Y., 1940.

[2] G. J. Bullen, *Nature*, **177**, 537 (1956); G. J. Bullen, R. Mason, and P. Pauling, *ibid.*, **189**, 291 (1961).

[3] B. K. Vainshtein, *Zh. Fiz. Khim.*, **26**, 1774 (1952).

[4] M. Nardelli, A. Braibanti, and G. Fava, *Gazz. chim. ital.*, **87**, 1209 (1957).

[5] M. A. Porai-Koshits and G. N. Tishchenko, *Kristallografiya*, **4**, 239 (1959); *cf.* R. H. Holm, *J. Am. Chem. Soc.*, **82**, 5632 (1960).

[6] F. K. C. Lyle, B. Morosin, and E. C. Lingafelter, *Acta Cryst.*, **12**, 938 (1959).

[7] L. M. Venanzi, *J. Chem. Soc.*, 719 (1958); N. S. Gill and R. S. Nyholm, *ibid.*, 3997 (1959); F. A. Cotton and D. M. L. Goodgame, *J. Am. Chem. Soc.*, **82**, 5771 (1960); D. M. L. Goodgame and F. A. Cotton, *ibid.*, **82**, 5774 (1960); D. M. L. Goodgame, M. Goodgame, and F. A. Cotton, *ibid.*, **83**, 4161 (1961); R. G. Hayter and F. S. Humiec, *ibid.*, **84**, 2004 (1962); M. D. Glonek, C. Curran, and J. V. Quagliano, *ibid.*, **84**, 2014 (1962).

[8] See R. H. Holm, *ibid.*, **82**, 5632 (1960), for numerous references.

[9] H. Irving, J. B. Gill, and W. R. Cross, *J. Chem. Soc.*, 2087 (1960).

[10] G. Maki, *J. Chem. Phys.*, **29**, 162 (1958).

[11] F. A. Cotton and J. P. Fackler, Jr., *J. Am. Chem. Soc.*, **83**, 2818 (1961).

insignificant steric hindrance; namely, the nickel complex of 4-amino-3-pentene-2-one [also called acetylacetone imine and its formal anion may be designated as acim; *i.e.*, the anhydrous nickel(II) chelate is Ni(acim)$_2$]. The only simple β-ketoimine complexes reported previously have been those of copper(II).[12] One possible reason for this is the easy hydrolysis of α,β-unsaturated β-ketoamines in the presence of metal ions and water to the corresponding β-diketone complexes.[13]

Experimental

Preparation of Compounds.—All compounds and solvents were of reagent grade or better quality.

4-Amino-3-pentene-2-one.—The compound was prepared by treating a solution of 50 g. of freshly distilled 2,4-pentanedione (Union Carbide) and 100 g. of toluene in a 250-ml. flask maintained at 65° with anhydrous ammonia for 2 hr. After separation from the water layer which forms, the oil was fractionally distilled. After the water and toluene in this layer were removed, the temperature rose to about 206–209°, the boiling point of the unsaturated aminoketone. The ligand undergoes a slight decomposition if distilled at atmospheric pressure; however, it can be distilled under reduced pressure (97 to 98° at 10.5 mm.); yield, 60–70%.

Bis-(4-amino-3-pentene-2-ono)-nickel(II).—Although solutions of aqueous nickel(II) ion and 4-amino-3-pentene-2-one do not yield precipitates directly, addition of sodium hydroxide, potassium hydroxide, or ammonium hydroxide gives a red precipitate. For example, a solution of 1.25 g. of $Ni(NO_3)_2 \cdot 6H_2O$ dissolved in 10 ml. of H_2O was added to 1.25 g. of solid 4-amino-3-pentene-2-one. The green solution yielded 0.79 g. of bis-(4-amino-3-pentene-2-ono)-nickel(II) upon the addition of 5.0 ml. of 6 *M* NH_4OH; yield, 72%; m.p., 246°; sublimation point (0.04 mm.), 85°.

Anal. Calcd. for $NiC_{10}H_{16}N_2O_2$: C, 47.10; H, 6.28; N, 10.99; mol. wt., 255. Found: C, 47.21; H, 6.29; N, 10.78; mol. wt., 247.

Ethanolic solutions of nickel salts and the unsaturated β-ketoamine slowly precipitate the same complex upon partial evaporation.

Bis-(2,4-pentanediono)-diaquonickel(II).—This complex was prepared by heating the aqueous nickel ion and β-ketoamine solution without the addition of base. The aqua colored complex is identical with that described earlier.[10,11]

Anhydrous Bis-(2,4-pentanediono)-nickel(II) Trimer.—Dehydration of the diaquo chelate by heat or heat and vacuum yielded the green anhydrous trimer of bis-(2,4-pentanediono)-nickel(II).[11]

Magnetic Measurements.—Magnetic susceptibilities have been measured on a standard Gouy balance consisting of an analytical balance, an electromagnet, and an associated power supply.

Spectral Measurements.—Ultraviolet and visible spectra of chloroform solutions of the chelates have been measured on a Cary Model 14 spectrophotometer using 1-cm. cells. Infrared measurements of the solid in KBr pellets at a concentration of *ca.* 0.5% have been made on a Perkin-Elmer Model 421 infrared spectrometer.

Molecular Weight.—The molecular weight has been determined on a vapor pressure osmometer (Mechrolab Model 301A) in chloroform. The instrument has been calibrated with chloroform solutions of benzil (molecular weight 201.2), which had been thrice recrystallized from ethanol.

Results and Discussion

Synthesis.—The nickel chelate has been synthesized in both aqueous and non-aqueous media. The resultant complex is very soluble in chloroform—the solution appears red if concentrated or yellow if dilute. The complex is somewhat less soluble in ethanol, pyridine, benzene, carbon tetrachloride, and nitromethane; it exhibits very low solubilities in ethyl ether and in aliphatic hydrocarbons; and it appears to be quite insoluble in water.

At elevated temperatures (*e.g.*, 90°) the complex reacts with water to give diaquobis-(2,4-pentanediono)-nickel(II), which also has been prepared from the α,β-unsaturated β-ketoamine by warming a solution of the ketoamine and nickel(II) ions rather than adding base. This hydrolysis reaction explains the inability of Collman[12c] to obtain the N-aryl chromium and cobalt chelates in aqueous solution at 80°. The β-diketone complex precipitates out of aqueous solution at a lower pH than the ketoamine complex. This allows the use of ketoamine which has partially hydrolyzed over a period of months or years to be used in the preparation of pure ketoamine complex by slowly making the solution basic in the presence of an excess of the ketoamine. Although the first fraction is a mixture of the chelates, the second is almost pure ketoamine, and the material recovered at pH values from 9 to 11 has the same melting point as that prepared from freshly synthesized ketoamine.

Spectral Characterization.—The red chelate, Ni(acim)$_2$, is diamagnetic in the solid state and exhibits a ligand field spectrum characteristic of the *trans*-NiO_2N_2 type compounds; *i.e.*, two allowed bands are noted (Table I) as in the nickel chelates of salicylaldoxime and salicylaldmethylimine,[14] both of which have been shown to possess the *trans* structure in the solid state[15] and have practically identical absorption spectra in the solid state and in $CHCl_3$ solution.[14] The *cis*-NiO_2N_2 planar complexes, such as bis-(acetylacetone)-ethylenediiminenickel(II) and bis-(salicylaldehyde)-ethylenediiminenickel(II), which must be *cis*-NiO_2N_2 by nature of their quadridentate, small ring structure, only exhibit one allowed ligand field band.[8, 14] These bands have been assigned by Maki.[14] The single band of the *cis*-NiO_2N_2 complexes has been attributed to the $^1A_1 \rightarrow {}^1B_1$ transition and the bands of the *trans* complexes as $^1A_g \rightarrow {}^1B_{3g}$ and $^1A_g \rightarrow {}^1B_{1g}$ for the low and high energy visible absorptions, respectively. A shift of $+1700$ to 2000 cm.$^{-1}$ (4.8 to 4.7 kcal./mole) is observed for the $^1A_g \rightarrow {}^1B_{3g}$ band of this complex relative to the salicylaldmethylimine and salicylaldoxime complexes, respectively, in the same solvent.

The visible spectrum of [Ni(acim)$_2$] is in accord with a *trans*-NiO_2N_2 type complex and the blue shift of both

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[12] (a) H. F. Holtzclaw, Jr., J. P. Collman, and R. M. Alire, *J. Am. Chem. Soc.*, **80**, 1100 (1958); (b) D. F. Martin, G. A. Janusonis, and B. B. Martin, *ibid.*, **83**, 73 (1961). Since completion of the manuscript, two papers have appeared on non-aqueous preparations of N-aryl derivatives of Cr^{III} and Ni^{II}, respectively: (c) J. P. Collman and E. T. Kittleman, *Inorg. Chem.*, **1**, 499 (1962); (d) W. Ludwig, *Helv. Chim. Acta*, **45**, 665 (1962).

[13] V. W. Gash, U. S. Patent No. 2,976,285, March 21, 1961.

[14] G. Maki, *J. Chem. Phys.*, **29**, 1129 (1958).

[15] L. L. Merritt, Jr., C. Guare, and A. E. Lessor, Jr., *Acta Cryst.*, **9**, 253 (1956); E. Frasson, C. Panattoni, and L. Sacconi, *J. Phys. Chem.*, **63**, 1908 (1959).

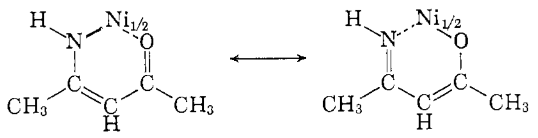
TABLE I

VISIBLE ABSORPTION BANDS OF PLANAR NICKEL(II) COMPLEXES

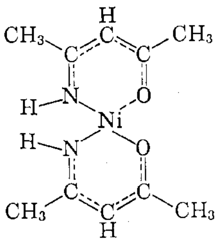
Ligand	Configuration	Absorption maxima[a]		Molar absorptivity	Ref.
		λ, mμ	ν̃, cm.$^{-1}$	ε	
Salicylaldoxime	*trans*	620	16,100	90	14
		(470)	(21,300)	(130)	
Salicylaldmethylimine	*trans*	610	16,400	100	14
		(490)	(20,400)	(150)	
4-Amino-3-pentene-2-one	(*trans*)	552	18,100	43	This study
		(435)	(23,000)	(85)	
Bis-(acetylacetone)-ethylenediimine	*cis*	565	17,700	80	8
Bis-(salicylaldehyde)-ethylenediimine	*cis*	(540)	(18,500)	(140)	8

[a] Shoulders are indicated in parentheses—values of λ, ν̃, and ε in those instances are only approximate.

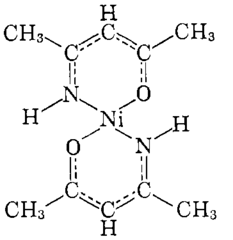
ligand field bands is in accord with stabilization of the type



that has been discussed previously for the parent α,β-unsaturated β-ketoamines.[16] The $^1A_g \rightarrow {}^1B_{3g}$ shift of the order of 2000 cm.$^{-1}$ is an appreciable amount. The hexafluoro derivative should have a red shift that would compensate for this, but difficulty in producing the fluorinated imines has been observed.[8] The *trans* structure also allows for minimum hydrogen–hydrogen interaction, maximum hydrogen bonding, and symmetry similar to the salicylaldehyde derivatives discussed above. However, there is no proof that some of the *cis* isomer does not exist if its absorption peak corresponds to either of the peaks of the *trans* complex. Absorption chromatography on alumina and Florisil has not allowed a separation of the two isomers, but this is not proof of only one isomer. The similarity of the two possible isomers is indicated in the structures shown below. It can easily be shown that the



cis



trans

cis isomer possesses only a very small dipole with respect to the *trans* isomer, as the nitrogen with a hydrogen further from the center of mass is almost equivalent to an oxygen atom. Because of this, dipole measurements have not been made.

In addition to the ligand field bands noted in the visible region, two overlapping, high intensity, electron transfer bands have been observed in the near-ultraviolet at 365 and at 349 mμ, the former a shoulder on the latter, so that true values for the peaks would require a more detailed analysis. These bands may be due to π → d (even t3), π → σ (even t3) and/or filled d → p_z. The difficulty and ambiguity of assigning the near-ultraviolet bands has been ably discussed by Jørgensen.[17] The spin forbidden transitions in the near-infrared are very weak[14] and were not detected in the solutions used in this study. The ε values of any such peaks must be less than 0.5.

Infrared Spectra.—The KBr pellet infrared spectrum of Ni(acim)$_2$ agrees well with the Nujol mull spectrum of the corresponding copper chelate reported by Holtzclaw and co-workers.[12a] The bands in cm.$^{-1}$ and band strengths (s, strong; m, medium; w, weak; sh, shoulder) for the nickel chelate (with the same for the corresponding copper chelate in parentheses) are: 3285 s, (3250 s); 2995 w, 2950 w, 2915 w (masked by Nujol); 1595 s (1585 s); 1550 w, 1520 w (1530 s); 1475 s, 1435 m, 1390 s (masked by Nujol); 1350 sh (1347 sh); 1250 m (1227 m); 1230 sh (1216 m); 1190 sh, 1180 s (1180 s, 1165 s); 1020 s (1017 s); 950 w, 935 s (932 s); 810 s (810 s); 790 sh (792 s); 755 s (758 s); 710 w (720 w); 680 m (685 w); 650 m. The close agreement is obvious.

The 3285–3250 cm.$^{-1}$ band, previously assigned as either an NH or an OH stretch,[12a] is undoubtedly an NH stretch—the weak absorption found in the N-methyl copper complex[12a] could be due to ammonia in the methylamine used to prepare the chelate. A strong OH seems unlikely for the unsaturated keto-amine chelates.

The infrared spectrum of Ni(acac)$_2$·2H$_2$O is also in agreement with other β-diketone spectra.[18]

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(16) G. O. Dudek and R. H. Holm, *J. Am. Chem. Soc.*, **84**, 2691 (1962), and references contained therein.

(17) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford, 1962, Chapter 9.

(18) J. Lewis and R. G. Wilkins, "Modern Coordination Chemistry," Interscience, New York, N. Y., 1960, p. 379.

(19) R. D. Archer and D. C. Young, unpublished results.