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Reactions of Copper(II) and Nickel(II) β-Keto Imine Complexes.[1] 3

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It has been reported[3] that Cu(baen), the copper(II) complex of the Schiff base condensation product of 2,4-pentanedione with ethylenediamine, reacts quickly and quantitatively at the methine position with isocyanates to yield mono- or diamides dependent solely on the relative stoichiometry of the reactants. By contrast, the analogous Ni(baen) was found to react very slowly and only with aryl isocyanates to yield only the monoamides. Since these reactions may be regarded as electrophilic substitution reactions,[4] the marked decrease in the reactivity of Ni(baen) relative to Cu(baen) could be due to the much greater acidity of the methine protons of Ni(baen) as has been found for similar compounds.[5,6]

If this tenet is correct, then electrophilic reactions with Ni(baen) should occur with more reactive electrophiles, e.g., those which bear strong electron-withdrawing substituents. As part of a continuing research program in this area, the reactions of the electron-deficient electrophiles, *p*-toluenesulfonyl isocyanate (tosNCO, A), diethyl azodicarboxylate (B), and dimethyl acetylenedicarboxylate (C), with Ni(baen) and Cu(baen) have been investigated. The results of these reactions are reported herein.

Experimental Section

Caution! *p*-Toluenesulfonyl isocyanate is toxic and is a powerful lachrymator and should be handled in an efficient fume hood and diethyl azodicarboxylate is potentially a thermally initiated explosive. The electrophiles were obtained from commercial sources and used as received. Solvents were dried by standard procedures. Spectral data were obtained as previously described.[3,7] Melting points obtained on a Meltemp apparatus are uncorrected. Room-temperature magnetic susceptibilities were determined by the Faraday method using $Hg[Co(NCS)_4]$ as calibrant.[8] Ligand diamagnetic corrections were calculated from Pascal's constants. Elemental analyses were performed by Chemalytics Inc., Tempe, Ariz. Satisfactory C, H, and N analyses were obtained for all new compounds.

The ligands and their copper(II) and nickel(II) complexes were prepared by published procedures[9] and purified as previously described.[3] All reactions were run in oven-dried glassware in essentially the same fashion. A mixture containing a 2:1 molar ratio of electrophile to complex in dry benzene was stirred magnetically at room temperature in a round-bottom flask fitted with a condenser and a $CaCl_2$ drying tube. Cu(baen) reacted quickly and exothermically with all three electrophiles while Ni(baen) reacted only at reflux. After 24 h, hexane was added to complete precipitation of the products, which were filtered and washed with hexane. Repeated recrystallizations from benzene/hexane or chloroform/hexane followed by vacuum-drying at room temperature afforded analytically pure samples. Pertinent physical properties of the products are listed in Table I. Ligand displacements were carried out with H_2S in chloroform as previously described.[3]

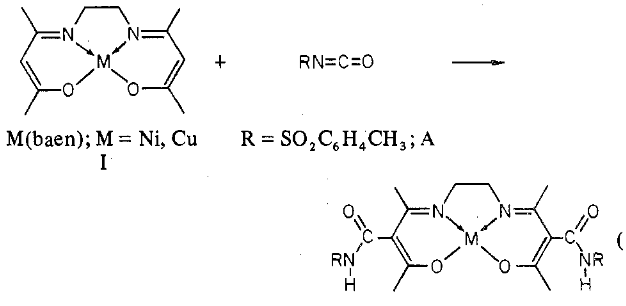
Table I. Physical Properties of the Compounds

Compd[a]	Mp, °C	% yield	Susceptibility, μ_B (K)	Form and color
Cu(baen·2A)	166–168	98	1.79 (293)	Lavender powder
Ni(baen·2A)-III[b]	146–149	90	Diamagnetic	Brown powder
Ni(baen·2A)-II[b]	111–114	20	Diamagnetic	Red-brown crystals
Cu(baen·2B)	148–150	70	1.79 (294)	Lavender powder
Ni(baen·2B)	159–162	59	Diamagnetic	Orange powder
Cu(baen·2C)	82–85	53	1.86 (296)	Brown powder
Ni(baen·2C)	96–98	40	Diamagnetic	Red crystals
Ni(bapn·B)	142–145	20	Diamagnetic	Red crystals

[a] baen ≡ the Schiff base condensation product of 2,4-pentanedione and 1,2-diaminoethane; bapn ≡ the Schiff base condensation product of 2,4-pentanedione and 1,2-diaminopropane; A ≡ *p*-toluenesulfonyl isocyanate; B ≡ diethyl azodicarboxylate; C ≡ dimethyl acetylenedicarboxylate. [b] See text for clarification of structure.

Results and Discussion

The reaction of *p*-tosyl isocyanate with Ni(baen) (eq 1) represents the first example of a complete reaction of an isocyanate with Ni(baen) to yield the diamide product. Previously reported isocyanate reactions between Ni(baen) and isocyanates yielded only the monoamide (R = phenyl, 1-naphthyl).[3] As anticipated, the electron-withdrawing ability of the *p*-tosyl group proved sufficient to promote the reaction. Not surprisingly, *p*-tosyl isocyanate reacted quickly and quantitatively with Cu(baen) yielding a product which is very similar in appearance and properties to other diamides[3] prepared by reaction of Cu(baen) with isocyanates. The addition of *p*-tosyl isocyanate to M(baen) is formally analogous to its addition to enol ethers to yield β-alkoxyacrylamides.[10] Elemental analyses of the Cu(baen·2A) and Ni(baen·2A) complexes establish that two molecules of tosyl isocyanate added to each molecule of M(baen). The absence of a methine C–H stretch[11] (Table II) in the infrared spectra of Cu(baen·2A) and Ni(baen·2A) (for Cu(baen), ν_{CH} = 1115 cm^{-1}, for Ni(baen), ν_{CH} = 1125 cm^{-1}) confirms that addition occurred at the methine position. However, the two compounds are not isostructural; the presence of amide ν_{N-H} (3150 cm^{-1}) and carbonyl $\nu_{C=O}$ (1595 cm^{-1}) in the infrared spectrum of the copper complex confirms that the bis secondary amide



M(baen); M = Ni, Cu
I

R = $SO_2C_6H_4CH_3$; A

(1)

M(baen·2A)
II

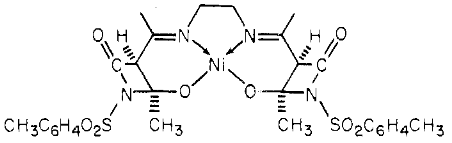
Table II. ^{1}H NMR Data[a] for the Products of Reaction of M(baen) with Electrophiles

Complex	δ(CH_3) (*J*, Hz)	δ($C_6H_4CH_3$)	δ(NH)	δ(C=C–H)	δ(CH_2)	δ(OH)	δ(C_6H_4)
H_2baen·2A	2.02 s, 1.94 s	2.46 s	5.27 bs	4.79 s[b]	3.41 m	10.55	7.47 (ABq)
Ni(baen·2A)-III	1.99 m	2.57 s	5.20 bs	4.82 s[b]	3.20 m		7.69 (ABq)
Ni(baen·2A)-II	1.87 s, 1.92 s	2.47 s	5.3 bs	4.9 s[b]	3.7 s		7.57 (ABq)
H_2baen·2B	1.26 t (7.5)[c]				3.56 m		
	2.20 s, 2.13 s		7.90 s		4.25 dq (7.5)[c]	10.55	
Ni(baen·2B)	1.26 t (7)[c]				3.10 s		
	2.08 s, 1.94 s		6.85 s		4.21 q (7)[c]		
Ni(bapn·B)	2.00 s, 1.93 s, 1.25 t (7)[c]				2.00 s		
	2.05 s, 1.87 s		6.58 s	5.04 s	4.18 q (7)[c]		
H_2baen·2C	2.00 s, 1.97 s, 1.76 s, 1.71 s						
	3.74 s,[d] 3.71 s[d]			6.85 s, 5.81 s	3.07 m		
Ni(baen·2C)	2.13 s, 2.06 s						
	3.83 s,[d] 3.81 s[d]			6.07 s	3.59 m		

[a] δ in ppm relative to internal $SiMe_4$; multiplets have standard NMR designations. [b] See text for explanation. [c] N-CH_2CH_3 moiety. [d] C(O)OCH_3 moiety.

product was formed, analogous to previously reported[3] Cu(baen)·2RNCO products. However, the infrared spectrum of the Ni(baen·2A) complex has significant differences from that of the corresponding copper complex. The expected amide N–H band is absent, and the carbonyl stretch is shifted in energy to 1748 cm^{-1}, which is too high in frequency for a secondary amide.[12]

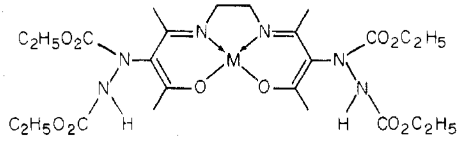
Among synthetic routes to β-lactams are reactions between olefins and chlorosulfonyl isocyanate.[13] Also, *p*-tosyl isocyanate reacts with some enol ethers to give similar products.[10] The carbonyl stretching frequency for a four-membered-ring exocyclic lactone-type carbonyl such as that in a β-lactam is normally found[14,15] in the vicinity of 1750 cm^{-1}. If a lactam-type structure obtains for the Ni(baen·2A) compound, the structure might well be III. Such a compound would not display an amide N–H stretch, and the carbonyl absorption would be raised in frequency to 1750 cm^{-1} or higher.



III

The ^{1}H NMR spectra (Table II) of these species do not permit unambiguous structure assignation. Sharp singlets with integrated intensities corresponding to slightly less than two protons are observed in the range appropriate to methine protons for both the Ni(baen·2A) complex and the H_2baen·2A ligand obtained by H_2S displacement. These resonances could be assigned to the methine hydrogen of the four-membered β-lactam ring, but the presence of what appears to be N–H resonances for the two compounds at δ 5.20 and 5.27, respectively, mitigates against the lactam formulation. The ^{13}C NMR data[16] suggest that both the β-lactam and amide or that several stereoisomers of the β-lactam are present as two resonances are observed for the methine carbon (δ 63.1, 99.9) and C–O(CH_3) (δ 21.1, 24.0) groups of Ni(baen·2A). Since the four-membered ring is regarded as an intermediate in the formation of secondary amides formed by electrophilic attack of tosyl isocyanate on unsaturated molecules,[10] it is possible that both species (β-lactam derivative and bis secondary amide) are present in Ni(baen·2A) and that H_2S displacement causes lactam ring opening. Refluxing a 50:50 CH_3OH–$CHCl_3$ solution of III for several hours apparently causes partial ring opening of the β-lactam as the ^{1}H NMR (Table II, Ni(baen)·2A-II) and infrared spectra of Ni(baen)·2A-III change considerably, viz., ν_{NH} 3200, $\nu_{C=O}$ 1590, and $\nu_{CO(amide)}$ 1670 cm^{-1}.

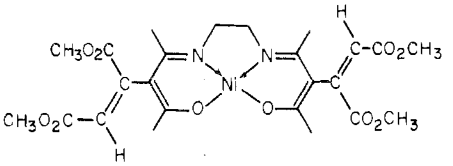
Electrophilic addition of diethyl azodicarboxylate (B) to M(baen) leads to hydrazine derivatives. Infrared (ν_{NH} 3290, ν_{CO} 1580, $\nu_{CO(amide)}$ 1752, 1705 cm^{-1}), ^{1}H NMR (Table II), and ^{13}C NMR spectral data support the dihydrazine structure (IV).



IV

The strong, sharp bands observed around 3300 cm^{-1} are assignable[15] to a hydrazine ν_{N-H}. The absence of a methine ν_{C-H} in the infrared spectra of the M(baen)·2B derivatives confirms that addition has occurred to both methine carbons of M(baen). The infrared spectrum of Ni(bapn·B) clearly shows that only one azodicarboxylate has added per molecule (confirmed by elemental analysis). The ^{1}H NMR spectral data (Table II) are suggestive of hindered rotation about the =C—N bond. The ^{1}H NMR (Table II) and ^{13}C NMR spectra of Ni(bapn)·B support the elemental analyses in that only monoaddition has occurred. To which side addition has occurred cannot be determined with certainty, but the ^{13}C NMR data clearly show that the addition is regiospecific as only two resonances are observed for the methine carbon (δ 115.7, 128.3). Four resonances would be expected for a mixture of isomers.

Dimethyl acetylenedicarboxylate (C) also readily adds to M(baen) to generate the bis adducts (V) and the infrared data, ^{1}H NMR data (Table II), ^{13}C NMR data, and elemental analyses are consistent with the proposed structure. The NMR spectral data suggest that both the cis and trans olefin isomers are present in roughly equal amounts and consequently that addition is not stereospecific. H_2S displacement of the ligand from M(baen)$_2$·2C produces only the trans isomer and this is probably the result of acid-catalyzed isomerization.



V

Acknowledgment. The financial support of the University of Nevada Research Advisory Board and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Registry No. Cu(baen·2A), 63848-35-1; Ni(baen·2A)-III, 63848-34-0; Ni(baen·2A)-II, 63848-33-9; Cu(baen·2B), 63848-32-8; Ni(baen·2B), 63866-31-9; Cu(baen·2C), 63848-31-7; Ni(baen·2C), 63848-30-6; Ni(bapn·B), 63848-29-3; H_2baen·2A, 63832-97-3;

H_2baen·2B, 63832-98-4; H_2baen·2C, 63848-88-4; Ni(baen), 36802-27-4; Cu(baen), 36885-37-7; A, 4083-64-1; B, 1972-28-7; C, 762-42-5; ^{13}C, 14762-74-4.

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Mössbauer Spectra of Np(V)-Cr(III) and Np(V)-Rh(III) Complexes[1]

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The aqueous Np(V) ion forms weak complexes with a number of trivalent cations;[2] however, the Np(V) ion forms particularly stable complexes with Cr(III)[3a] and Rh(III)[3b] ions. The Np(V)-Cr(III) and Np(V)-Rh(III) complexes can be separated from the remaining uncomplexed ions by ion exchange.[3a] The suggested structure for these complexes involves substituting the NpO_2^+ ion for a water molecule in the first coordination sphere of the hexaaquochromium(III) and hexaaquorhodium(III) ions. The Np(V) ion is believed to enter the coordination sphere axially and is coordinated through an oxygen atom to the Cr(III) or Rh(III) ion. Normally, the linear NpO_2^+ ion coordinates around its equator, so the axial coordination of these complexes presents an unusual environment for the Np(V) ion. This paper reports a study of the Np(V) in the Cr(III) and Rh(III) complexes by Mössbauer spectroscopy. Because Cr(III) is paramagnetic ($3d^3$, high spin) and Rh(III) diamagnetic ($4d^6$, spin = 0), a contrast in magnetic effects is also expected.

Experimental Section

NpO_2 was dissolved in hot 6 M HNO_3, and the resulting ^{237}Np concentration was assayed radiometrically. The Np(V):Np(VI) ratio was then determined spectrophotometrically. Np(VI) was reduced to Np(V) by adding the calculated amount of KI, and the solution was filtered to remove precipitated iodine. Neptunium(V) hydroxide was then precipitated by adding aqueous ammonia. The hydroxide was filtered and washed until free of ammonia and dissolved in 1 M $HClO_4$ to yield the Np(V) stock solution.

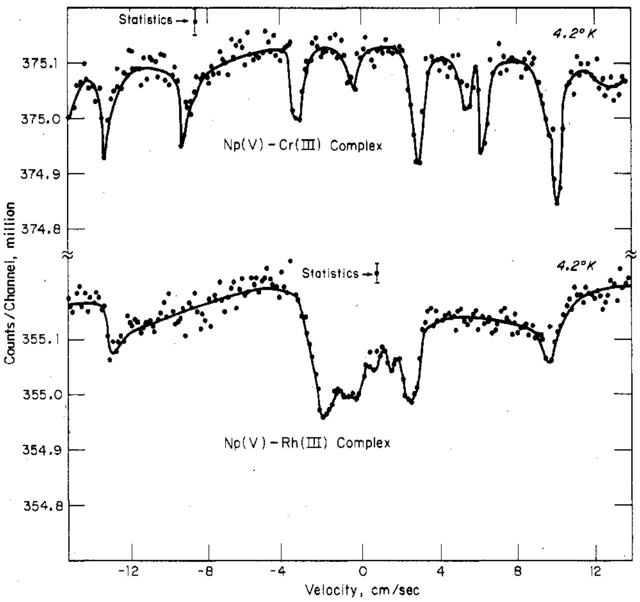

Figure 1. Mössbauer spectra of Np(V)-Cr(III) and Np(V)-Rh(III) complexes.

Solid $Rh(H_2O)_6(ClO_4)_3$ was prepared for the Np(V)-Rh(III) complex by fuming rhodium trichloride (Research Organic/Inorganic Chemical Corp.) in concentrated perchloric acid.[4] Chromium chloride (Fisher Chemical Co.) was dissolved in water, and the solution was allowed to stand at room temperature for 1 week. The mixture of chromium(III) hydroxides was then precipitated with NaOH, and the hydroxides were washed with water and dissolved in a minimum volume of 3 M $HClO_4$ to produce a perchlorate solution of mixed $Cr(H_2O)_6^{3+}$, $Cr(H_2O)_5Cl^{2+}$, and $Cr(H_2O)_4Cl_2^+$ ions.

The Np(V)-Rh(III) complex was prepared[3b] by dissolving an approximately equimolar amount of solid $Rh(H_2O)_6(ClO_4)_3$ in a solution of Np(V) and by allowing the resulting solution to stand at room temperature for 2 weeks.[3b] The Np(V)-Cr(III) complex was prepared by adding the solution of mixed Cr(III) cations to an Np(V) solution, and the mixture was allowed to stand 2 weeks.

Absorption spectra of these solutions with a Cary 14 spectrophotometer showed the Np(V)-Rh(III) solution had about 50% of the Np(V) as the Np(V)-Rh(III) complex. The Np(V)-Cr(III) solution showed about 30% of the Np as the Np(V)-Cr(III) complex. No Np(IV) or Np(VI) species were detected in the spectra.

Mössbauer spectra of the complexes were then determined from the complexes absorbed on Dowex[5] 50 cation-exchange resin. Dowex 50 resin, either 2 or 4% cross-linked, 100-200 mesh, was graded to remove fines and was then washed with concentrated HCl, water, and 2 M $HClO_4$. After the resin was washed with 2 M $HClO_4$, it was again washed with water and then packed in a 6-mm-diameter × 3-cm glass column. A solution containing either the Np(V)-Rh(III) or Np(V)-Cr(III) complex was passed through the column and eluted with 2 M $HClO_4$ to remove Np(V) and Rh(III) or Cr(III) from the resin. More of the solution of the complexes was then passed through the column and Np(V) and Rh(III) were again eluted until the resin was saturated with the Np(V)-Rh(III) or Np(V)-Cr(III) complex. The resin was forced from the column mechanically, and excess solution was removed by a vacuum on a Büchner funnel. The resin was then packed tightly in a plastic holder which was sealed for Mössbauer measurements, as previously performed.[6]

Results and Discussion

The Mössbauer spectra measured at 4.2 K of the Np(V)-Cr(III) and Np(V)-Rh(III) complexes absorbed on Dowex 50 cation-exchange resin are shown in Figure 1. (The curves in these spectra were not computer fits.) The spectrum of the Np(V)-Cr(III) complex has the major features of a spectrum combining large magnetic and small quadrupole splitting, similar to that of neptunium(V) oxalate,[7] with some weak satellite lines. These weak satellite lines suggest a minor