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Inner Complexes. VI. Mixed Chelates from Thiopicolinamides and β-Diketones

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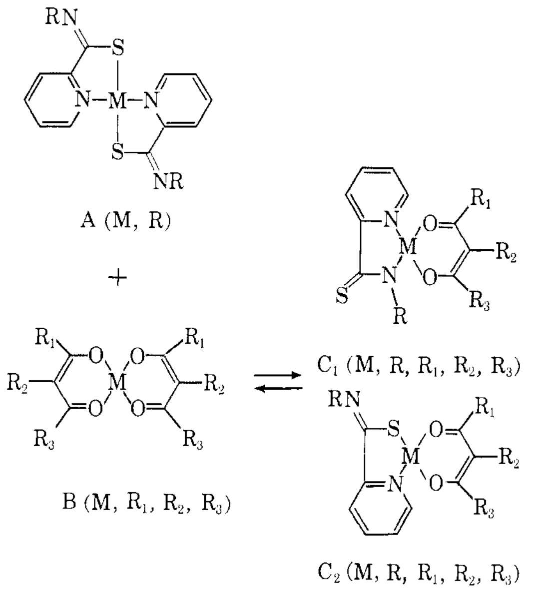
Copper(II) and nickel(II) chelates of N-alkylthiopicolinamides interact with β-diketonates of the corresponding metal to form mixed chelates in greater than statistical concentration. For systems in which the N-alkyl group is a radical of low steric bulk the mixed chelates have a square-planar configuration around the central metal atom and the thioamide group bonds to the metal atom through the nitrogen atom.

Introduction

In the course of studies on the preparation of chelate polymers it was observed that copper(II) or nickel(II) chelates of various thiopicolinamides, A, interact with β-diketone chelates, B, to produce mixed chelates, C.[2] Some studies on the structure and stability of these new chelates were made in solution, and a number of these labile mixed chelates were isolated as crystalline solids. The results of these studies are presented herein.



A (M, R)

B (M, R_1, R_2, R_3)

C_1 (M, R, R_1, R_2, R_3)

C_2 (M, R, R_1, R_2, R_3)

Experimental

All temperatures are uncorrected. Gouy measurements were made by Dr. L. Vaska at Mellon Institute. N.m.r. measurements were carried out under the direction of Dr. W. F. Beach of this laboratory. X-Ray data were supplied by W. D. Niegisch and K. LaGattuta of this laboratory.

Preparation of Mixed Chelates C.—Green bis(2,4-pentanedionato)nickel(II) (129 mg., 0.005 mole) and bis(N-(n-butyl)-thiopicolinamidato)nickel(II) (223 mg., 0.005 mole) were heated to reflux in 3 ml. of benzene. Petroleum ether (10 ml.) was added to the solution and the precipitated orange mixed chelate, 327 mg. (93%), was recovered by filtration. Recrystallization from heptane gave dark red crystals, m.p. 155–157°, while lighter colored platelets were obtained from benzene–petroleum ether which melted partially at 110–120°, resolidified, and remelted at 155–157°. Ebullioscopic molecular weight determinations in methylene chloride gave a molecular weight of 346, calcd. 351. Other chelates were similarly prepared (Table I).

Preparation of Dimetal Mixed Chelates.—A mixture of bis-(N-(n-butyl)thiopicolinamidato)nickel(II) (445 mg., 0.001 mole) and 2,4,12,14-tetraketopentadecane (123 mg., 0.0005 mole) in 5 ml. of chloroform was allowed to stand for 1 hr. and precipitated with petroleum ether. The product was recrystallized from benzene–cyclohexane to give a pure dimetal mixed chelate, m.p. 118–120°.

Anal. Calcd. for $C_{36}H_{48}O_4N_4S_2Ni_2$: C, 54.57; H, 6.28; mol. wt., 770.26. Found: C, 54.77; H, 6.37; mol. wt. (osmometric, 1% in chloroform, 37°), 826 ± 68.

Mixed Chelates from Thiopicolinamide.—Thiopicolinamide (0.7 g., 0.005 mole) and bis(2,4-pentanedionato)nickel(II) (1.25 g., 0.004 mole) were mixed in 30 ml. of chloroform to yield a red-brown precipitate of bis(thiopicolinamidato)nickel(II). The filtrate from the above reaction was precipitated in petroleum ether to give a red chelate believed to be the mixed chelate C (Ni, H, CH_3, H, CH_3) (Table I). The infrared spectrum in a potassium bromide disk showed absorptions at 3215 cm.$^{-1}$ and in the 6–7 μ region a shoulder at 1610, 1574, 1527 (β-diketone), 1488, and 1431 cm.$^{-1}$. No absorption at 1075–1080 cm.$^{-1}$ was observed. The ultraviolet spectrum had an inflection at 423 mμ and maxima at 362, 343, 329, and 258 mμ.

Spectra.—The ultraviolet spectra were obtained on chloroform solutions having concentrations of approximately 10^{-3}–10^{-4} M using a Cary Model 14 recording spectrophotometer. Typical spectra for chelates having a relatively nonbulky R group are shown in Figure 1. Typical values are for C (Ni, n-C_4H_9, CH_3, H, CH_3) [λ_{max} in mμ (log ϵ in l. mole^{-1} cm.$^{-1}$)]: 398 (3.74), 371 (3.77), 326 (3.86), and 263 (4.32) and for C (Cu, n-C_4H_9, CH_3, H, CH_3): 359 (3.77), 302 (4.22), and 289 (4.25).

The visible spectra of the copper β-diketone chelates were recorded on the same instrument using chloroform solutions of varied concentration. The centers of the lowest frequency maxima were for B (Cu, CF_3, H, CH_3) 14,970 cm.$^{-1}$, (Cu, C_6H_5, H, CH_3) 15,198 cm.$^{-1}$, (Cu, CH_3, H, CH_3) 15,337 cm.$^{-1}$, (Cu, CH_3, CH_3, CH_3) 15,503 cm.$^{-1}$. These values were the centers of very broad maxima. Various measurements duplicated these values to within ±2 mμ. These values differ somewhat from other literature values.[3]

All infrared spectra were taken on a Perkin-Elmer Model 21 spectrophotometer (Figure 2).

The proton n.m.r. spectra were obtained on deuteriochloroform solutions using a Varian A-60 spectrometer at ambient temperature with a tetramethylsilane (TMS) internal standard. Chemical shifts downfield from TMS in c.p.s. (and multiplicity where resolved) for the aliphatic protons are C (Ni, n-C_4H_9, CH_3, H, CH_3) 192 (3), 87, 75, 56 (3), (117 (1), 332 (1) acetylacetonate peaks); C (Ni, i-C_4H_9, CH_3, H, CH_3) 182 (2), broad absorption around

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[2] Some recent references on mixed chelates include: K. O. Watkins and M. M. Jones, *J. Inorg. Nucl. Chem.*, **24**, 809 (1962); D. L. Leussing, *J. Am. Chem. Soc.*, **85**, 231 (1963); L. C. Thompson and J. A. Loraas, *Inorg. Chem.*, **2**, 89 (1963).

[3] R. L. Belford, A. E. Martell, and M. Calvin, *J. Inorg. Nucl. Chem.*, **2**, 11 (1956); R. L. Belford, M. Calvin, and G. Belford, *J. Chem. Phys.*, **26**, 1125 (1957).

TABLE I

MIXED CHELATES C (R_1, R_2, R_3)$C_3O_2M[(NR),S]CC_5H_4N$

R	R_1	R_2	R_3	M.p., °C.	Calcd., % C	Calcd., % H	Found, % C	Found, % H
				Copper Chelates				
CH_3	CF_3	H	CH_3	196–197 dec.	39.18	3.01	39.63	3.02
n-C_4H_9	CH_3	H	CH_3^a	187–188 dec.	50.47	5.65	50.71	5.67
n-C_4H_9	CF_3	H	CH_3	180–181 dec.	43.95	4.18	44.45	4.33
n-C_4H_9	CH_3	CH_3	CH_3	175–177 dec.	51.94	6.00	51.88	6.07
n-C_4H_9	CH_3	H	$OC_2H_5^b$	160–161 dec.	49.79	5.75	49.33	5.55
n-C_4H_9	CF_3	H	OC_2H_5	171–173 dec.	43.67	4.35	43.45	4.08
n-C_4H_9	CH_3	Cl	CH_3	175–176 dec.	46.15	4.91	46.10	4.93
n-C_4H_9	CH_3	H	C_6H_5	171–172 dec.	57.46	5.31	57.28	5.31
n-C_4H_9	CF_3	H	CF_3	135–140 dec.	38.84	3.04	38.76	3.01
i-C_4H_9	CF_3	H	CH_3	168–170 dec.	43.95	4.18	44.37	4.29
i-C_4H_9	CH_3	CH_3	CH_3	172–174 dec.	51.94	6.00	51.82	6.05
s-C_4H_9	CF_3	H	CH_3	180–181 dec.	43.95	4.18	44.40	4.49
s-C_4H_9	CH_3	CH_3	CH_3	181–183 dec.	51.94	6.00	52.04	6.19
t-C_4H_9	CH_3	CH_3	CH_3	177–179 dec.	51.94	6.00	51.88	6.19
				Nickel Chelates				
H	CH_3	H	CH_3	*ca.* 225 dec.	44.78	4.07	44.43	4.27
CH_3	CH_3	H	CH_3	*ca.* 250 dec.	46.64	4.57	46.84	4.79
n-C_4H_9	CH_3	H	CH_3^c	155–157	51.31	5.74	51.23	5.69
n-C_4H_9	C_6H_5	H	$C_6H_5^d$	260–264 dec.	63.18	5.09	62.91	5.05
n-C_4H_9	$C_3H_6^e$	H	CH_3	162–164	54.14	5.88	54.11	6.17
i-C_4H_9	CH_3	H	CH_3	160–161	51.31	5.74	51.70	5.88
s-C_4H_9	CH_3	H	CH_3	210–213 dec.	51.31	5.74	51.12	6.03
t-C_4H_9	CH_3	H	CH_3	234–236 dec.	51.31	5.74	51.33	6.01

[a] Calcd.: N, 7.85. Found: N, 7.83. [b] Calcd.: N, 7.26. Found: N, 7.44. [c] Calcd.: N, 7.89. Found: N, 8.16. [d] Calcd. Ni, 12.35. Found: Ni, 12.1. [e] $CH_2{=}C(CH_3)H$–, mol. wt. calcd., 377; found (osmometric 1% in $CHCl_3$, 37°), 369.

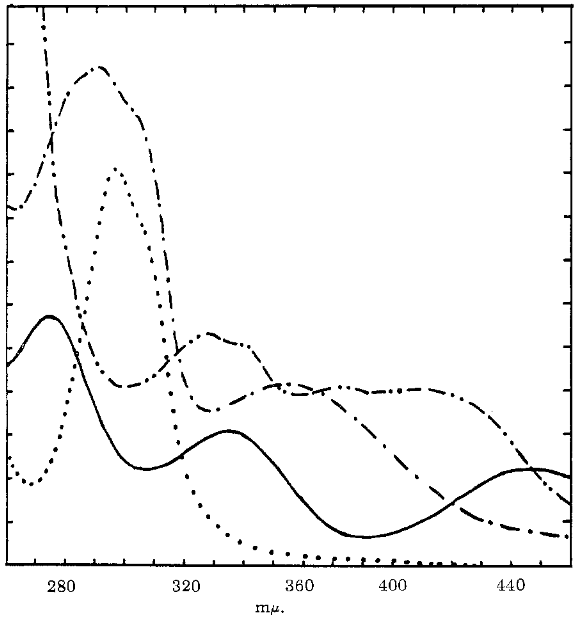

Figure 1.—Ultraviolet spectra in chloroform of (a) A (Cu, n-C_4H_9), 0.0005 *M* ———; (b) B (Cu, CH_3, H, CH_3), 0.0005 *M* ......; (c) C (Cu, n-C_4H_9, CH_3, H, CH_3), 0.001 *M* —·—·—; (d) C (Ni, n-C_4H_9, CH_3, H, CH_3), 0.001 *M* — — ··.

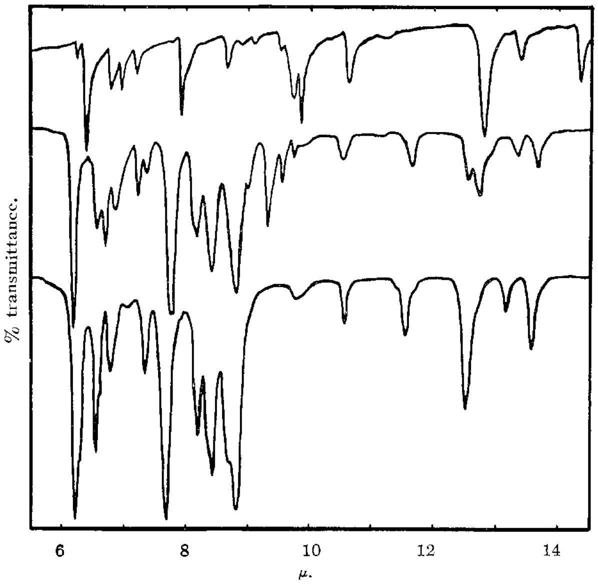

Figure 2.—Infrared spectra of equal molar concentration of (top) A (Cu, CH_3), (middle) C (Cu, CH_3, CF_3, H, CH_3), and (bottom) B (Cu, CF_3, H, CH_3) in potassium bromide.

120, 61 (2), 117 (1), 330; C (Ni, s-C_4H_9, CH_3, H, CH_3) 237, broad absorption 80–125, 71 (2), 54 (3), 114 (1), 326 (1); C (Ni, t-C_4H_9, CH_3, H, CH_3) 90, 114, 326; C (Ni, CH_3, CH_3, H, CH_3) 119 (1), 165 (1) (NCH_3), 333 (1).

Magnetic Moments.—Gouy balance measurements on C (Ni, n-C_4H_9, CH_3, H, CH_3) in chloroform solutions gave $\mu_{eff} = 0.56$ B.M., which was invariant over a period of several days. The same compound in benzene or chloroform solution with 2% tetramethylsilane standard gave $\mu_{eff} = 0.0$–0.62 B.M. by the method of Evans.[4] Using this n.m.r. method uncorrected for density, a magnetic moment of 0.0 was obtained for benzene solutions of C (Ni, CH_3, CH_3, H, CH_3) and 1.5 B.M. for C (Ni, t-C_4H_9, CH_3, H, CH_3).

X-Ray Diffraction Powder Patterns.—X-Ray diffraction patterns were obtained on finely ground samples using the copper Kα line and a 57.3-mm. radius camera with a 3-hr. exposure. The *d* spacings and intensities are for C (Cu, n-C_4H_9, CH_3, H, CH_3): 8.50 (mw), 7.90 (mw), 6.80 (s), 6.40 (m), 5.85 (m), 5.50 (mw), 4.80 (mw), 4.45 (m), 3.68 (ms), 3.50 (vs), 3.15 (w), 2.95 (vw); for C (Ni, n-C_4H_9, CH_3, H, CH_3): 8.50 (mw), 7.90 (mw), 6.80 (s), 6.40 (m), 5.90 (m), 5.60 (m), 5.20 (vw), 4.83 (mw), 4.50 (ms), 3.98 (w), 3.75 (ms), 3.58 (vs), 3.15 (vw), 2.93 (w).

Equilibrium Constants.—Equilibrium constants were calcula-

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(4) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

ted for the mixed copper chelates in chloroform at 25° using the absorption maximum of the starting thiopicolinamide chelates near 440 mμ and independently for several examples at the mixed chelate absorption near 360 mμ. Absorptions at both of these wave lengths for A, B, and C appeared to obey Beer's law. Ratios of A:B in most systems were varied from 1:10 to 1.2:1. The total concentration used, based on the concentration of C at a 1:1 ratio, was about 2×10^{-4} *M* for the determinations based on the 360 mμ peak and 2×10^{-4} and 1×10^{-3} *M* using the peak near 440 mμ. Each determination was repeated using a different solution at least twice and the 1:1 values were checked using recrystallized mixed chelate where possible. The molar absorptivity of the mixed chelate was determined using a sufficiently large excess of weakly absorbing β-diketone chelate B (ratios up to 100:1 B:A) and correcting for the excess B in solution in the reference beam. For the less stable mixed chelates the molar absorptivities thus obtained were used to calculate the equilibrium constants, the equilibrium constants thus obtained were used to correct the molar absorptivity of C, and the equilibrium constant was redetermined. This technique was repeated until constant equilibrium constants were obtained. For the values reported herein the molar absorptivities of mixtures of A, B, and C remained constant over periods of hours after an initial equilibration period of up to 5 min. Some mixed chelates such as C (Cu, *n*-C_4H_9, CH_3, H, OC_2H_5) decomposed significantly under these conditions and meaningful equilibrium constants could not be obtained.

Results

Mixed chelates C (Table I) are formed by heating in solution equimolar amounts of the starting chelates A and B. The conversion is particularly facile for the copper chelates, in agreement with their lability, occurring even upon mechanically grinding the two chelates in potassium chloride. Mixed chelate formation can be observed visually as the copper mixed chelates are green in the solid phase, and the nickel chelates, in agreement with a square-planar configuration, are red.[5] Some exceptions to these colors are found in the mixed chelates where R is a bulky group such as a *s*- or *t*-butyl group.

Molecular weight measurements on several of the mixed nickel chelates C and also on the dinickel chelate from 2,4,12,14-tetraketopentadecane and N-*n*-butylthiopicolinamide indicate them to be nonassociated in relatively dilute solutions and are in agreement with mixed chelate formation. Magnetic studies on the nickel chelates C (Ni, R, CH_3, H, CH_3) in solution indicate the mixed chelates (at least those in which R is a primary radical) to be essentially square-planar. The small observed magnetic moments for some of these nickel chelates may be due to some distortion from planarity in C but more likely to equilibration to form paramagnetic B. A correlation of the structure of the nickel and copper mixed chelates was made using X-ray powder diffraction patterns which show the crystalline chelate C (Cu, *n*-C_4H_9, CH_3, H, CH_3) to be isomorphous with the corresponding nickel chelate.

In the 300–500 mμ region the mixed chelates have absorptions uniquely different from those of the parent chelates A or B (Figure 1). The most characteristic absorption of the copper mixed chelates (where R is a primary or other sterically nonbulky group) occurs at about 360 mμ. It is found in all the green mixed chelates except when this area is masked by a stronger ligand absorption as in C (Cu, *n*-C_4H_9, CH_3, H, C_6H_5). The position of this peak is relatively insensitive to changes in the β-diketone ligand and can be attributed to an absorption involving the thiopicolinamide ring. A second maximum or shoulder occurs near 300 mμ and can be attributed to a π–π^* transition of the β-diketone ligand.[6] It is absent in the mixed chelates from β-ketoesters, the parent chelates of which absorb maximally at much lower wave lengths. The data do not distinguish whether this absorption maximum is attributable to the undissociated mixed chelate or to the parent chelate B formed by the reverse of the formation reaction. This latter effect is present in the spectra of all mixed chelates and corrections for it have not been made. A third peak generally found at 265–290 mμ is probably due to a maximum found in the same region in the thiopicolinamides and their chelates[7] modified by strong β-diketone absorptions. The spectra of the nickel mixed chelates differ considerably in some aspects from those of the copper mixed chelates but have similar maxima (or shoulders) near 370 mμ and in the 260–270 mμ range. In addition to peaks in the 320–340 mμ region, the nickel mixed chelates have unique maxima or shoulders at about 390–400 mμ. In this latter region relatively strong absorptions have previously been reported which have been attributed to the nickel chelate[8] rather than any ligand absorption. The spectra of the copper and nickel mixed chelates, where R is a bulky group such as *s*- or *t*-C_4H_9, differed from those described above in varying degrees dependent on the metal and β-diketone ligand.

In the infrared region of the spectrum one can readily identify most of the β-diketone chelate absorptions in the spectra of the mixed chelates (Figure 2). The most characteristic absorptions of B occur in the 6.2–6.7 μ region, and these bands (or band)[9] also exist in the spectra of the mixed chelates although their molar extinctions are about half those of the parent chelates B, in agreement with the concentration of the chromophore in the mixed chelate. Some shifts in the positions of the β-diketone absorptions are noted, such as the absorption at 1610 cm.$^{-1}$ in B (Cu, CF_3, H, CH_3) is shifted to 1620 cm.$^{-1}$ in C (Cu, CH_3, CF_3, H, CH_3). Only a few of the absorptions of A are also found relatively unchanged in the mixed chelate C, the pyridine ring proton wagging frequency being an exception, being found at 780–790 cm.$^{-1}$. For the mixed chelates in which R is a hydrocarbon radical of low steric bulk, new bands appear, and characteristic of this effect is a medium intensity absorption found at 1075–1080 cm.$^{-1}$. Other characteristic bands of the parent chelate A apparently disappear upon coordination in a mixed chelate system (R is small). Significant in this latter group is the absorption near 1565 cm.$^{-1}$. Although

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[5] R. S. Nyholm, *Chem. Rev.*, **53**, 263 (1953).

[6] (a) J. Charette, G. Neirynck, and P. Teyssie, *J. Phys. Chem.*, **65**, 735 (1961); (b) J. P. Fackler, F. A. Cotton, and D. W. Barnum, *Inorg. Chem.*, **2**, 97 (1963).

[7] R. W. Kluiber, *ibid.*, **4**, 829 (1965).

[8] J. E. Mills and D. P. Mellor, *J. Am. Chem. Soc.*, **64**, 181 (1942); K. Sone, *ibid.*, **75**, 5207 (1953).

[9] R. P. Dryden and A. Winston, *J. Phys. Chem.*, **62**, 635 (1958).

this region is obscured by absorptions of many β-diketones, in the system based on C (Cu, CH_3, CF_3, H, CH_3) (Figure 2), its absence in mixed chelates C, where R is a radical of low steric bulk, can be seen. Because of its position, this 1565 cm.$^{-1}$ band in A can be assigned to a C=N stretching frequency of the thioamide group.[7]

Proton magnetic resonance spectra of mixed nickel chelates show some shifts in all of the peaks due to aliphatic protons from those of the starting chelates A.[7] The most significant of these is found in the absorptions due to the two protons on a methylene group attached directly to the thioamide nitrogen. This peak is shifted upfield by about 0.5 p.p.m. As the R group becomes bulkier, increased formation of the parent A and paramagnetic B with consequent line broadening and the presence of additional peaks is observed. Thus, chloroform-*d* solutions of C (Ni, *s*-C_4H_9, CH_3, H, CH_3) show peaks due to the parent system A (Ni, *s*-C_4H_9) and the position of the highly split resonance peak due to the proton attached to the methinyl group bonded to the amide nitrogen could not be exactly determined. Best estimates indicate it to be shifted upfield about 0.1 p.p.m.

Equilibrium constants, K_{AB}, based on the system $A + B \rightleftarrows 2C$ were evaluated for the copper chelates using several β-diketone systems in combination with thiopicolinamides having R groups of varying size (Table II). These constants were obtained spectroscopically using the absorption maximum of A at 430–450 mμ and independently checked in several cases using the mixed chelate maximum at 360 mμ. This latter determination was not as satisfactory as that obtained at 430–450 mμ due to the rapidly changing and relatively large absorptivity of the parent chelate A in the 360 mμ region. In calculating the equilibrium constants it was assumed that all activity coefficients were unity and that only one mixed chelate species was present in solution. This assumption is supported (but not proven) by the presence of an "isosbestic point" in the 400–410 mμ range (after correcting for excess B).

TABLE II

EQUILIBRIUM CONSTANTS FOR THE FORMATION OF C (Cu, R, R_1, R_2, R_3) IN CHLOROFORM AT 25°

$$A + B \underset{}{\overset{K_{AB}}{\rightleftarrows}} 2C$$

	(R_1, R_2, R_3)			
R	CF_3, H, CH_3	C_6H_5, H, CH_3	CH_3, CH_3, CH_3	CH_3, H, CH_3
CH_3	4300	...	1400	325
n-C_4H_9	440	250	125	43
i-C_4H_9	240	...	39	14.3
s-C_4H_9	100	...	9.3	5.6
t-C_4H_9	210	...	9.8	6.5
$C_6H_5CH_2$	...	...	...	45

Discussion

The structure of the mixed chelates in which R is a radical of relatively small steric requirements (*i.e.*, methyl, isobutyl, benzyl, and perhaps phenyl) is probably C_1. Magnetic data for these mixed nickel chelates and X-ray powder pattern correlation of a nickel(II) and copper(II) mixed chelate (R = *n*-butyl) indicate these compounds to have essentially a square-planar configuration around the central metal atom. (The nickel and copper thiopicolinamide chelates A[7] and the β-diketone chelates B[10] when not associated are also square-planar.) For such a configuration the stability of C_2 relative to A and B would not be expected to be greatly influenced by the size of the R group. However, in square-planar C_1 with trigonal hybridization of the thioamide nitrogen, the R group interacts sterically with the adjacent oxygen and considerable steric hindrance can be expected when R is a *t*-butyl group. An analogous situation is found in the salicylaldimines.[11] In agreement with structure C_1 the spectral and equilibrium data show that the structure and position of equilibrium of the mixed chelates are directly dependent on the size of R for both the copper and nickel mixed chelates. Thus for systems where R is *s*- or *t*-butyl the mixed chelates appear to have an alternate structure, possibly C_2. The C_1 structure for mixed chelates where R is sterically small is supported by infrared data which indicate the absence or diminution in intensity of what may be a thioamide C=N stretching mode at about 1565 cm.$^{-1}$. The n.m.r. data are in agreement with structure C_1 for ligands with sterically small R groups. However, lesser amounts of C_2 admixed and in equilibrium with C_1 cannot be excluded by the present data.

The principal driving force for the formation of mixed chelates in this system appears to be the ability of the thiopicolinamide ligand to coordinate with the metal in the mixed chelate through the thioamide nitrogen rather than through the sulfur. The parent chelate A can only exist in the N_2S_2 form, as the alternate structure in which the metal is bonded to the trigonal thioamide nitrogen is prohibited by F strain.[7] Nitrogen–sulfur linkage isomerization in the thiocyanate complexes has recently been extensively discussed,[12] and the electronic and steric factors envoked to rationalize the effects found for thiocyanate should be equally applicable to the N,S linkage isomerization in the thioamides. A complicating factor in thioamide complexes is that coordination through nitrogen can result either in a tetrahedral or trigonal nitrogen. The former structure results in loss of the thioamide resonance and should, therefore, be energetically less favorable.[7,13] In view of these factors it is not surprising that the literature contains examples of coordination of ambidentate ligands to Cu(II) and Ni(II), some of which involve metal–nitrogen bonding and some

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(10) R. B. Roof, Jr., *Acta Cryst.*, **9**, 781 (1956); F. A. Cotton and J. P. Fackler, *J. Am. Chem. Soc.*, **83**, 2818 (1961).

(11) R. H. Holm and K. Swaminathan, *Inorg. Chem.*, **2**, 181 (1963); L. Sacconi, P. L. Orioli, P. Paoletti, and M. Ciampolini, *Proc. Chem. Soc.*, 255 (1962).

(12) Leading references are: F. Basolo, W. H. Baddley, and J. L. Burmeister, *Inorg. Chem.*, **3**, 1202 (1964); C. K. Jørgensen, *ibid.*, **3**, 1201 (1964).

(13) R. J. Niedzielski, R. S. Drago, R. L. Middaugh, *J. Am. Chem. Soc.*, **86**, 1694 (1964).

metal–sulfur bonding.[14] For the apparently less complicated thiocyanato system, Ni(II) does coordinate through the nitrogen,[15] in agreement with the hard acid–hard base concept.[16] A similar explanation appears reasonable for the nitrogen coordination in the mixed chelates described herein. In the present state of refinement and extension of the data, no evidence has been found for any electronic influence of the other coordinating group on the nature of the linkage isomerization in the thiopicolinamide, although the mixed chelates in which R is a sterically bulky group present some unsolved inconsistencies. Minor factors which may influence the stability of the mixed chelate include F strain interactions between the metal-bonded sulfur atom and the proton on the 6 position of the pyridine ring (stabilizing) and the loss of sulfur-metal multiple bonds in the mixed chelate (destabilizing). These effects are probably small.

The dependence of the equilibrium constants on the nature of the β-diketone ligand in the copper(II) system can be interpreted at least in part on steric grounds. Thus electron-withdrawing groups such as $-CF_3$ remove electronic charge from the metal-bonded oxygens, thus reducing their effective steric bulk either directly or by decreased solvation or by increased metal–oxygen distance with consequent increase in stability of the mixed chelate. It is interesting to note that the copper chelates C (Cu, *s*- or *t*-C_4H_9, CF_3, H, CH_3) are green solids with solution spectra showing maxima around 360 mμ. An attempt was made to correlate the equilibrium data with the λ_{max} of the lowest frequency d–d transition of the copper β-diketonates and also with the half-wave polarographic reduction potential[17] of these chelates. (Apparently these latter two physical constants correlate better with one another than with the formation constants[18] with which they are normally compared, at least for the few values obtained in the present research.) For the limited data available, as the frequency of the d–d transition increases or the half-wave potential decreases the equilibrium constant for mixed chelate formation goes through a minimum. Such a result is in qualitative agreement with the electrostatic theory of mixed chelate formation of Kida.[19]

The nickel chelate system presents an additional complication in mixed chelate formation. Bis(2,4-pentanedionato)nickel(II) and presumably other green nickel β-diketone chelates exist in solution as octahedrally-coordinated trimers (or their equivalent),[20] the equilibrium concentration of monomer being quite small. Mixed chelate formation, therefore, must proceed at the expense of one nickel oxygen bond per β-diketone ligand and the over-all equilibrium should be concentration dependent. These factors may account for our inability to isolate pure mixed nickel chelates of β-ketoesters and fluorinated β-diketones by the simple techniques introduced herein.

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[14] Several examples include: L. Cavalco, M. Nardelli, and G. Fava, "Abstracts, Seventh International Conference on Coordination Chemistry," Stockholm, Sweden, June 1962, p. 211; P. Rây and A. K. Choudhury, *J. Indian Chem. Soc.*, **27**, 673 (1950); S. N. Poddar and P. Rây, *ibid.*, **29**, 279 (1952).

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A Search for Configurational Activity Effects in the Hydrolysis of the (+) and (−) Forms of the Arsenic(V)–Catechol Complex

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The rates of hydrolysis of the (+) and (−) forms of the arsenic(V) complex with catechol have been examined in solutions containing 0, 5, 10, 15, and 20% sucrose. These were determined by a method using conductance measurements which requires no assumptions to be made about the effect of one optically active species on the rotatory power of another when both are present in the same solution. Although the presence of the sucrose has a considerable effect on the rates, this effect is the same for the (+) and (−) forms, within the limits of experimental error. This system thus gives no indication of the occurrence of configurational activity effects. Some of the general factors bearing on the occurrence of such effects are delineated.

In an earlier study[1] we reported that the hydrolysis of the (+) and the (−) forms of the arsenic(V)–catechol complex proceeded at the same rates in the presence of various added optically active electrolytes. The over-all reaction here is

$$H[As(O_2R)_3(H_2O)] \rightleftharpoons R(OH)_2 + H[OAs(OR)_2]$$

where $R(OH)_2$ is catechol. These rate measurements were carried out polarimetrically. A point of conten-

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