

sensitive to small errors.^{18,19} Charles²⁰ has reported that large differences are possible as in the case of the determination of the ΔH for the reaction of Mg(II) with EDTA, where the ΔH values disagree even as to the sign. The discussion of the thermodynamics of formation is based on calorimetric data since the accuracy of this method is inherently higher.

The $-\Delta H^\circ$ value for 2-pyridylcarbinol is 23.32 (Table II), while that for 6-methyl-2-pyridylcarbinol is 13.53 kcal./mole. This lower enthalpy value for the 6-methyl compound shows a weakening of the metal-ligand bond caused by the methyl group in the 6-position. A similar, though less pronounced, effect is noticed when comparing 2-(β -hydroxyethyl)pyridine ($-\Delta H^\circ = 13.82$ kcal./mole) with 2-(β -hydroxyethyl)-6-methylpyridine ($-\Delta H^\circ = 12.43$ kcal./mole).

The entropy change for the 2-pyridylcarbinol Cu(II) chelate is +9.4 e.u., while that for the 6-methyl compound is +38.1 e.u. (Table II). The much more favorable entropy effect of the latter compound may be

(18) F. Basolo and R. K. Murmann, *J. Am. Chem. Soc.*, **76**, 211 (1954).

(19) J. W. Cobble, *J. Chem. Phys.*, **21**, 1451 (1953).

(20) R. G. Charles, *J. Am. Chem. Soc.*, **76**, 5854 (1954).

attributed to "solvation effects"²¹ in which the methyl substituent in the 6-position tends to shield the central metal ion from solvent molecules, thus increasing the total number of particles in the solution. This increased randomness is not sufficient to counteract the steric hindrance, and, as seen from Table I, the 2-pyridylcarbinol chelate is more stable.

The same trend is observed when comparing the 2-(β -hydroxyethyl) chelates. However, a much smaller increase in entropy is noted for 2-(β -hydroxyethyl)-6-methylpyridine (+41.2 e.u.) as compared to 2-(β -hydroxyethyl)pyridine (+38.5 e.u.). This smaller increase seems to indicate that the shielding of the metal atom by the methyl group is less effective in chelates containing six-membered rings.

(D) **Conclusions.**—The results of this study show that the presence of a methyl group in a sterically blocking position in these compounds causes both a bond-weakening effect and a favorable increase in entropy. The stability values indicate that the entropy effect is not large enough to overcome the bond weakening caused by steric hindrance.

(21) W. D. Johnston and H. Freiser, *Anal. Chim. Acta*, **11**, 201 (1954).

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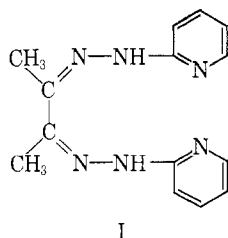
Quadridentate Chelate Compounds. IV. Metal Complexes from Butane-2,3-dione Bis(2'-pyridylhydrazone)

BY BARRY CHISWELL¹ AND FRANCIS LIONS

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Some planar quadridentate chelate compounds have been prepared from butane-2,3-dione bis(2'-pyridylhydrazone) and transition metal salts favoring square-planar four-coordination [Cu(II), Ni(II), and Pd(II)]. The complex cations of these complex salts could be doubly deprotonated by alkalis and the planar neutral complexes obtained.

Lions and Martin² in 1958 reported the interaction of biacetyl and 2-pyridylhydrazine to yield the osazone I and showed that it could function as a planar quadridentate chelating agent. At the same time they reported as an isolated phenomenon the partial de-



protonation of the complex cations of a cobalt(III) complex salt containing chelate groups derived from the α -pyridylhydrazone of an aldehyde. Subsequent work³ has shown the generality of this deprotonation

process. It seemed, therefore, to be of value to study some of the complex salts formed from the α -pyridyl osazones of 1,2-diketones and their behavior toward alkalis.

α -Dicarbonyl compounds such as glyoxal, biacetyl, and cyclohexane-1,2-dione readily yielded osazones with α -pyridylhydrazine. The present paper reports studies with I.

Using accurate drawings and accepting the usual values for atom sizes and bond angles the arrangement of the molecule of I shows that spatially it would appear to be able to function only imperfectly as a planar quadridentate ligand. Nevertheless, experiment shows that it does so function, giving the salts II with salts of bivalent metals such as copper(II), nickel(II), and palladium(II) (Table I). Treatment of these salts with alkalis leads to deprotonation of their complex cations and formation of the neutral complexes III (Table II). These latter are all soluble in organic solvents and, during preparation, are con-

(1) Petroleum Research Fund Fellow, University of Sydney.

(2) F. Lions and K. V. Martin, *J. Am. Chem. Soc.*, **80**, 3858 (1958).

(3) J. F. Geldard and F. Lions, *ibid.*, **84**, 2262 (1962); *Inorg. Chem.*, **2**, 270 (1963); B. Chiswell and F. Lions, *ibid.*, in press.

TABLE I
 BUTANE-2,3-DIONE-BIS(2'-PYRIDYLHYDRAZONE)METAL SALTS(II)

No.	Formula	Color	Conductivity, ohms ⁻¹ cm. ²	Analyses									
				Calcd.					Found				
				C	H	N	M	X	C	H	N	M	X
1	[C ₁₄ H ₁₆ N ₆ Cu](ClO ₄) ₂	Olive-green	56.8	31.6	3.0	15.8	12.2		31.3	3.2	15.7	12.1	
2a	[C ₁₄ H ₁₆ N ₆ Ni](ClO ₄) ₂	Yellow-brown	57.3	31.8	3.0	15.9	11.1		32.0	3.1		11.2	
2b	[C ₁₄ H ₁₆ N ₆ Ni]Cl ₂	Yellow	56.8	42.2	4.0	21.1	14.8	17.8	42.4	4.1	20.3	14.8	17.6
2c	[C ₁₄ H ₁₆ N ₆ Ni]Br ₂	Yellow	56.3	34.5	3.3	17.3	12.1	32.8	34.7	3.5	17.1	12.3	32.9
2d	[C ₁₄ H ₁₆ N ₆ Ni]I ₂	Orange	54.9	28.9	2.8	14.5	10.1	43.7	29.8	2.1	14.1	10.2	44.0
2e	[C ₁₄ H ₁₆ N ₆ Ni](SCN) ₂	Yellow	56.9	43.3	3.6	25.3	13.2		43.3	3.8	24.5	13.1	
3	[C ₁₄ H ₁₆ N ₆ Pd]Cl ₂ ·0.5H ₂ O	Green	54.3	37.0	3.7	18.4	23.4	15.6	37.1	4.0	17.9	23.7	15.7
4	[C ₁₄ H ₁₆ N ₆ Zn(H ₂ O) ₂](SO ₄)	Cream	54.6	35.3	4.2	17.7	13.8		35.1	4.9	17.3	13.6	

 TABLE II
 BUTANE-2,3-DIONE-BIS(2'-PYRIDYLHYDRAZONATO)METAL "NEUTRAL" COMPLEXES (III)

No.	Formula	Color	Analyses							
			Calcd.				Found			
			C	H	N	M	C	H	N	M
5	[C ₁₄ H ₁₄ N ₆ Cu]C ₂ H ₆ O ^a	Black	52.6	5.1	21.7	16.6	52.5	4.6	21.9	16.3
6	[C ₁₄ H ₁₄ N ₆ Ni]	Black (red streak)	51.6	4.3	25.8	18.1	52.0	4.5	25.2	18.0
7	[C ₁₄ H ₁₄ N ₆ Pd]	Green	45.2	3.8	22.6	28.6	45.2	4.0		28.4

^a 1 mole of acetone of crystallization.

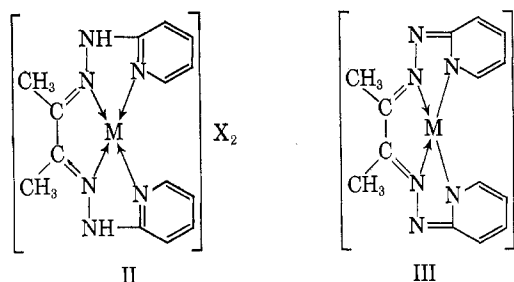


TABLE III

Compound	Ultraviolet peaks, m μ	Visible, m μ	Infrared (N-H band), cm. ⁻¹
1	238 (ϵ 328)	325	3500
1 + alkali	246 (ϵ 283.5)	387	
5	246.5 (ϵ 283.6)	388	None
2	247 (ϵ 318)	408	3430
2 + alkali	242 (ϵ 293)	377	
6	241.5 (ϵ 293)	378	None
3			3325
7			None

veniently extracted from aqueous mixtures into benzene.

Spectral studies in both the visible and ultraviolet ranges (Table III) indicate that addition of alkali to ethanolic solutions of the complex copper(II) and nickel(II) salts causes structural changes and alteration in the positions of peaks, the new values corresponding with those obtained by observation of ethanolic solutions of the pure neutral compounds. Similarly, study of the infrared spectra of these same salts and the corresponding neutral complexes as well as the complex palladium(II) chloride and the neutral palladium(II) complex show quite clearly that stretching absorptions due to the N-H bond which are present in the infrared spectra of the salts have disappeared from the spectra of the corresponding neutral complexes (Table III).

Some further comments are necessary. Thus, it was possible to obtain a complex zinc(II) sulfate from I. Analysis showed the presence of two water molecules. Four-coordinate zinc(II) complexes are generally tetrahedral so that this complex sulfate would seem to be a *trans* diaquo six-coordinate compound. However, it was not found possible to isolate a pure deprotonated neutral complex from it.

Several nickel (II) salts were prepared in an endeavor to ascertain whether halide ions affected the coordination process between metal and ligand. However, no unusual results were noted. Interaction of I with co-

balt(II) perchlorate in ethanol led to formation of a very dark red compound, but this decomposed in air to an oily tar within a few hours. The structural similarities of such planar cobalt(II) complexes to some of the oxygen-absorbing chelates of cobalt strongly suggests that this transformation is due to oxygen uptake.

With only one or two exceptions none of these complex compounds melted below 300°. The values determined for conductivities (Table I) are what would be normally expected. All the complexes were diamagnetic with the exception of the two copper complexes (I, 1.87 B.M.; 5, 1.84 B.M.).

Experimental

Tables I and II summarize some of the experimentally obtained data on these compounds. The solvents used for recrystallization and the complexes recrystallized from each solvent were (1) 50% aqueous ethanol (1, 2a, 2b, 2c, 2e, 3, and 4); (2) acetone (5); (3) benzene (6 and 7). The salt 2d was not recrystallized.

Conductivities were determined in analytical reagent quality nitrobenzene solution at 25.0 \pm 0.1° using a Philips Philoscope and platinum plated electrodes of the dip type. The neutral complexes 5, 6, 7, and 8 had zero conductivities.

Butane-2,3-dione bis(2'-pyridylhydrazone) (I) was prepared from biacetyl and 2-pyridylhydrazine as previously described.²

Preparation of Complex Salts.—Variations in methods of preparation were as follows: (A) A solution of I (2 molar proportions) in ethanol was treated with an aqueous solution of the metal perchlorate (1 molar proportion). Evaporation followed by

cooling caused deposition of the crude product (salts 1, 2a). (B) This was similar to A except that a salt other than a perchlorate was used (salts 2b, 2c, 2d, and 2e). (C) This also was similar to A but the metal salt used was K_2PdCl_4 .

Preparation of Neutral Complexes.—(D) An aqueous solution of the metal salt (1 molar proportion) was treated with slightly more than the theoretical amount of ammonium hydroxide solution to form the water-soluble complex ammine salt. This solution was then added to a solution of the ligand I (2 molar proportions) in ethanol. The neutral complex III separated after evaporation and cooling (neutral complexes 5, 6, and 7). (E) A

solution of the complex salt II (prepared by A, B, or C) in ethanol-water was treated with 5 *N* sodium hydroxide solution in slight excess, and the neutral complex was extracted into benzene, washed with water, dried with anhydrous sodium sulfate, and the solvent removed (neutral complexes 5, 6, and 7).

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THE UNIVERSITY OF SYDNEY, SYDNEY, AUSTRALIA

Tridentate Chelate Compounds. IV. Metal Complexes from α -Diketone Mono- α -pyridylhydrazone Type Ligands

BY BARRY CHISWELL,¹ FRANCIS LIONS, AND MURIEL L. TOMLINSON²

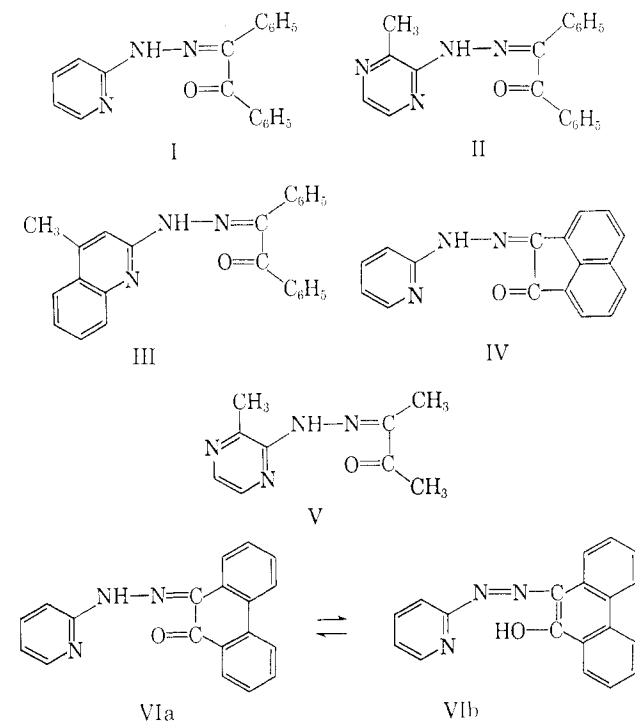
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Several α -diketones, such as benzil, acenaphthenequinone, and phenanthraquinone, have been condensed with *N*-heterocyclic hydrazines of the amidrazone type, such as 2-pyridylhydrazine, to form monohydrazones. In neutral alcoholic solution these hydrazones react with salts of certain transition metals as tridentate chelating agents with loss of the imino hydrogen atom. In acid solutions the deprotonation can be prevented and the ligands appear then to function only as bidentate chelating agents. Studies are reported most fully for copper(II) and nickel(II) salts. A red organic-solvent-soluble six-coordinate sodium complex is also reported. The structures of all these complexes have been deduced after consideration of infrared, ultraviolet, and visible spectra, conductivity measurements, and magnetic studies.

It is well known that whereas certain types of α -dicarbonyl compounds—and, as precursors of such compounds, α -ketols—readily yield osazones when caused to react with substituted hydrazines, such as phenylhydrazine, some α -diketones are extremely reluctant to form osazones. In these instances reaction usually stops at the monophenylhydrazone stage. We have found that benzil, phenanthraquinone, and acenaphthenequinone react with 2-pyridylhydrazine to give the mono-(2-pyridylhydrazone) only. There was no evidence of osazone formation, and we have been unable to prepare bis-(2-pyridylhydrazones) by any method³ from these ketones. Similar behavior was observed when 4-methyl-2-quinolyldiazine was caused to react with benzil or when 3-methyl-2-pyrazinylhydrazine was caused to react with benzil. A monohydrazone was prepared also from this latter hydrazine and biacetyl. However, it was also possible to obtain the osazone from these two reactants under forcing conditions.

The six mono-(2-azaaryl)hydrazones I–VI (Table I) are all capable of functioning as tridentate chelating agents. The typical red “azo” color of VI when contrasted with the yellow to orange colors of the other hydrazones suggests that it should be formulated as a 2-pyridineazophenol (VIb) and that its properties could well resemble those of the well-known 1-(2'-

pyridineazo)-2-naphthol and 4-(2'-pyridineazo)resorcinol. The interrelationships of the quinonehydrazone



and azophenol forms in such compounds as VI have often been studied.⁴

(1) Petroleum Research Fund Fellow, University of Sydney.

(2) Visiting Petroleum Research Fund Fellow at University of Sydney from University of Oxford.

(3) Cf., e.g., H. Ingle and H. H. Mann, *J. Chem. Soc.*, 67, 611 (1895).

(4) For an account, see, e.g., H. Zollinger "Diazo- and Azochemistry," Interscience Publishers, Inc., New York, N. Y., 1961, pp. 322–327.